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Wet Removal Rates and Mechanisms

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HAZARDOUS AIR POLLUTANTS: WET REMOVAL RATES AND MECHANISMS

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ABSTRACT

Fourteen hazardous organic air pollutants were evaluated for their potentials to be wet deposited by precipitation scavenging. This effort included a survey of solubilities (Henry's-Law constants) in the literature, measurement of solubilities of three selected species, development and documentation of a general deposition model (MPADD) which includes dry deposition and plume depletion, and performance of scavenging field experiments to provide a data base for testing the model. Solubility parameters (dimensionless ratio of aqueous concentration to air concentration) for ethylene oxide, nitrobenzene, and methyl chloroform were measured in rainwater at two temperatures each; the values obtained agreed generally with previous work except those for methyl chloroform, which were somewhat lower than previous experimental and calculated values. Four field experiments were conducted: three using nitrobenzene and one involving methyl chloroform. Agreement of measured concentrations with model-calculated values was good for nitrobenzene, despite larger than desired experimental uncertainties during two of the releases. Analytical difficulties resulted in only a few measurements of methyl chloroform rainwater concentrations; these however, were in general agreement with model calculations and expectations on the basis of its much lower solubility than that of nitrobenzene. These results and sample test runs of the Multi-Pollutant Atmospheric Deposition and Depletion (MPADD) model, including dry deposition estimates, show that wet deposition should have little effect on plumes of non-reactive hazardous gases within kilometers of their sources.

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SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency is undertaking a program to evaluate the environmental fate of a number of possibly hazardous organic chemicals which are currently being considered for regulation. One aspect of this study concerns the atmospheric behavior of these hazardous air pollutants (HAP), in particular their behavior leading to removal from the atmosphere by chemical reaction and wet and dry deposition. The present project is focused on wet removal by precipitation scavenging of fourteen organic chemicals, listed in Table 1.

The primary objective of the project is:

- to provide a reliable and convenient methodology for evaluating the wet removal of the listed pollutants, which is based on a sound understanding of the pertinent atmospheric interactions.

The project is divided into three major components, each of which provides necessary input to the fulfillment of the primary goal:

- Deposition modeling
- Solubility determinations
- Field experiments.

Development of the deposition model is the major vehicle for establishing the methodology required by the overall objective. Although the main thrust of the project is in the area of precipitation scavenging, the model was required to be versatile, including dry deposition and provisions for incorporation of chemical reactions and a variety of source configurations. Furthermore, the output should be

TABLE 1. Hazardous Air Pollutants of Present Interest

Material		Molecular wt.
Acetaldehyde	CH_3CHO	44.1
Acrylonitrile	CH_2CHCN	53.1
Carbon Tetrachloride	CCl_4	153.8
Chloroform	$CHCl_3$	119.4
Cresols	$CH_3C_6H_4OH$[a]	108.1[b]
Epichlorohydrin	CH_2OCHCH_2Cl	92.5
Ethylene Oxide	CH_2OCH_2	44.1
Methyl Chloroform (1,1,1-trichloroethane)	$C(CH_3)Cl_3$	133.4
Methylene Chloride	CH_2Cl_2	84.9
Nitrobenzene	$C_6H_5NO_2$	123.1
Perchloroethylene	C_2Cl_4	165.8
Phenols	C_6H_5OH[a]	94.11
Phosgene	$COCl_2$	98.9
Polychlorinated Biphenyls	$(C_6H_5)_2$([c])	154+

[a]And derivatives [b]p-cresol
[c]Chlorine adducts

compatible with models describing the fate of pollutants after deposition, and a user's manual with complete description and computer code listing provided. This modeling effort is being shared with a companion project entitled: Hazardous Air Pollutants: Dry Deposition Phenomena. Dry deposition modeling will be described in detail in the final report of that project.

For precipitation scavenging, the most important physical property of a non-reactive pollutant gas is the solubility. Thus, reliable values for solubilities are essential inputs to the deposition model, and this component of the project includes a literature search for known Henry's Law constants - calculated and measured - of the listed HAP. This search provides guidance for selection of a few species for which solubility measurements would be made, and a means for selection of candidate HAP for field scavenging experiments.

The third component of the project involves field measurements of wet deposition. These provide a data base for testing the performance of the deposition model, and an independent measure of scavenging of organic materials for general application to the study of HAP atmospheric behavior.

Conclusions of the study and recommendations for further research are given in Section 2 of this report. The following three sections detail progress toward accomplishment of the project's goals, in each of the three components noted above. All relevant experimental data are presented in the Appendices.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The Multi-Pollutant Atmospheric Deposition and Depletion (MPADD) code is a significant advance in the area of modeling precipitation scavenging and dry deposition of hazardous and other types of pollutants. It contains a new timesaving integration scheme, and is versatile in that it produces both dry and wet fluxes, describes depletion of the pollutant plume, and can accept a variety of plume model and chemical reaction mechanisms. Although the primary application of MPADD in the present context is for below-cloud scavenging and dry deposition from plumes, it is capable of including in-cloud processes. Applications during the present project were to gaseous species with physical properties and chemical reaction behavior that could be described relatively simply. As our knowledge of the properties of hazardous air pollutants increases, MPADD should be tested and the relevant subroutines refined accordingly.

The literature of solubility behavior of the candidate list of fourteen hazardous air pollutants is not extensive, and measurements of Henry's Law constants do not involve as wide a range of temperatures as one would like for atmospheric assessments. Experimental values for acetaldehyde and acrylonitrile apparently do not exist. Due to unanticipated costs associated with preparations for field scavenging experiments, measurements of solubility during the present project were limited to three species: ethylene oxide, nitrobenzene and methyl chloroform. These measurements were performed in rainwater and filled temperature gaps in the Henry's Law constant record for these species.

The results generally agreed with previous work except for methyl chloroform, where the measured solubility parameters were somewhat lower than previous results.

Solubility is a very important property influencing precipitation scavenging behavior. It is therefore important that more measurements be made on species of particular interest. In particular, data at more temperatures are needed, and attention should be given to identification and study of liquid phase reaction mechanisms. Such reactions, which could occur much faster than gas phase reactions, may significantly alter concentrations of hazardous materials scavenged by precipitation.

Four controlled-release experiments employing nitrobenzene and methyl chloroform were conducted during the early months of 1983. This component of the project absorbed a larger than anticipated portion of the project resources - mainly due to technical problems associated with release of the chemicals - but the results were valuable in providing data under realistic atmospheric conditions for testing the MPADD model and solubility information. Although a difficulty with the release solution led to above-normal uncertainty in released mass during two of the three nitrobenzene experiments, agreement with MPADD predictions was good - generally within a factor of two - for this species. However, the calculated rainwater concentrations were generally higher than those observed. This result could be due to the mass-transfer description in the model or to uncertainty in nitrobenzene solubility, which is apparently a strong function of temperature. Unfortunate analytical problems led to a loss of many of the concentration measurements from the methyl chloroform release. The surviving values, while not sufficient to provide a measure of cross-plume integrated flux, do show

that the scavenging follows the predicted behavior in being much less efficient than nitrobenzene due to much lower solubility.

The results of the field study provide strong support for the validity of the MPADD model, but additional experiments should be performed, using particular species of environmental concern and/or species with chemical properties different from those heretofore tested. Although the technology of release of liquid organic compounds for purposes of investigating atmospheric behavior of the vapors is well in hand as a result of this project, we recommend, where possible, that measurements be performed as well in the vicinity of existing routine releases. The scavenging measurements could be made in conjunction with gas-phase measurement and source characterization studies at these locations. Although it may be impractical to conduct detailed scavenging studies at accidental release or spill sites, the collection of a few precipitation samples - using appropriate procedures - could provide valuable information not otherwise obtainable.

SECTION 3

DEPOSITION MODELING

In this section we present a general description of the MPADD (Multi-Pollutant Atmospheric Deposition and Depletion) model, and simple examples of its use for hazardous air pollutants. MPADD simulates the behavior of a single or multicomponent plume of airborne material as it is transported, reacted, scavenged, and dry-deposited downwind. The code is intended to provide a convenient and useful method for practical assessment of the behavior of airborne hazardous air pollutants.

MPADD is a somewhat distant descendant of the reactive plume-scavenging model, SMICK (1), although these are totally separate codes and there is little resemblance between the two. MPADD represents a substantial advancement beyond SMICK; in particular,

- MPADD utilizes a newer and much more efficient procedure for numerical integration (2). This substantially decreases computer-time requirements for code execution.
- MPADD includes dry deposition as well as wet deposition.
- MPADD accounts for gaseous plume depletion.
- MPADD is much more streamlined and modularized, allowing faster operation and enhanced versatility.

The above features represent considerable improvements over MPADD's predecessors, and regardless of the nature of the source configuration (eg. tall stacks, urban areas, disposal sites, ...) the MPADD framework produces a much more convenient method for general plume scavenging and deposition calculations. MPADD essentially renders SMICK obsolete, and should be employed for all situations where SMICK formerly would have been utilized.

The following subsections segregate macroscopic and microscopic features of the model and basic relationships and governing equations are presented briefly. A more complete description of the model, including listings, identification of variable names, and a detailed example of its use is presented in the User's Manual, accompanying this report.

MACROSCOPIC FEATURES

Macroscopic features of the deposition model are summarized in Figure 1. Here the ensemble of gas-phase pollutants is emitted as a plume (or composite of individual plumes) from some sort of generalized source region, whereupon they experience advection, mixing, possible chemical reaction, and dry and wet deposition. The dry deposition flux is calculated for each pollutant as the product of its gas-phase concentration at ground-level and its dry deposition velocity.* Wet removal is computed by allowing precipitation to fall through the plume along trajectories determined by the raindrops' fall speeds and the mean wind. Typically the raindrop spectrum is discretized into a number of size categories, and total delivery at a receptor point (XG, YG, ZG) is computed by evaluating the composite of individual contributions over this spectrum.

Uptake of pollutants by individual falling drops is computed via integration of appropriate material-balance equations. Each drop is allowed to assume an initial "background" concentration (possibly zero), arising from equilibrium with a background air concentration, or as a result of liquid-phase reaction in cloud water. In the present MPADD formalism, this background is presumed uniform for all time and x,y

*A more complete description of dry deposition features of MPADD will be presented in the final report of the concurrent project: Hazardous Air Pollutants: Dry Deposition Phenomena.

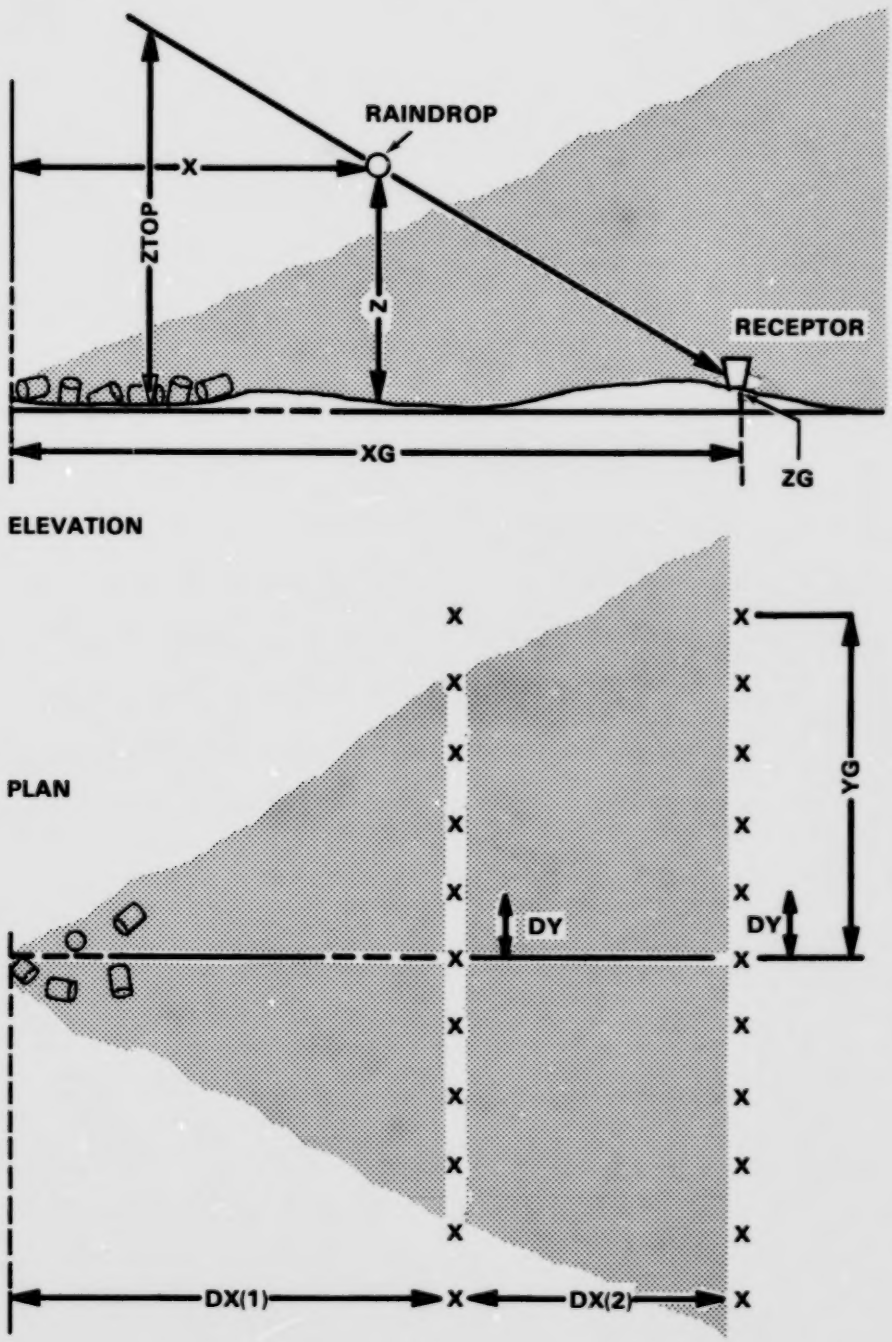

Figure 1. Schematic elevation and plan views of model layout.

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locations. Before integration occurs, the code determines an appropriate starting point for the integration (ZTOP), which ensures that the drop is above the plume. The code then divides the trajectory into appropriately-spaced increments and proceeds with the numerical integration, terminating whenever the receptor is encountered.

The code's operation is based upon the establishment of some arbitrary datum point (x=0, y=0, z=0). For symmetric plumes the plane defined by y=0 normally would define the centerplane of the plume, but this is not absolutely necessary. Similarly, x=0 and z=0 usually relate strongly to the source location, but there is considerable latitude regarding this choice. For the specific plume model utilized in this report (which is indeed symmetric about the y axis), y=0 is taken to coincide with the centerplane; x=0 and z=H (source height) are taken as the coordinates of the furthest upwind extremity of the source.

Normal operation of the code is to initially advance downwind by a distance DX(1), numerically integrating the dry deposition flux in the downwind direction to account for dry removal in that increment. An array of lateral wet deposition values is then computed at the current x-location, and these values are integrated numerically to estimate plume depletion arising from wet deposition to this point. At each downwind distance, the gas-phase plumes are modified by adjusting their effective source terms to account for upwind removal. Upon completion of this step the code advances the increment DX(2) to a new downwind distance, and the process is repeated until a normal exit from the code is accomplished.

The possibility of modular subroutine exchange allows the user considerable flexibility in choosing a suitable plume model. Essential requirements of any plume model acceptable to this code are itemized as follows:

1. The subroutine defining the plume model must print, upon demand, an appropriate alphanumeric label, describing its nature.
2. Upon demand the subroutine must provide values for XDMIN, ZTOP, DY, and the number of receptor locations to the left (y negative) and right (y positive) of the y=0 axis (code variables NYR and NYL). XDMIN is the downwind distance at which to begin calculating dry deposition.
3. The subroutine must, upon appropriate interrogation, provide ground-level concentrations and dry-deposition fluxes for each plume species.
4. The subroutine must be capable of providing concentrations of plume species at any point x, y and z upon request.

The specific plume submodel utilized for examples in this report is the Gaussian solution to the diffusion equation. It was chosen on the basis of general applicability to problems associated with hazardous air pollutants, and compatibility with the approach taken to calculate dry deposition in the EPA Gaussian plume computer code PAL-DS(3). Since the accurate calculation of scavenging and dry deposition of pollutants depends heavily on the accuracy of the model for the atmospheric dispersion, other more complicated models may be more appropriate for some applications.

MICROSCOPIC FEATURES

The previous subsection described gross aspects of how the plume and deposition features are calculated in the MPADD code. This section addresses more specific aspects of the rain-plume interactions, with particular emphasis on the behavior of individual raindrops.

It is appropriate to note major differences between chemical species in the plume and those contained within the falling precipitation, and to indicate the MPADD system for distinguishing between these classes. In the code and in the following discussion we shall adopt the naming convention given in Table 2. As can be noted here, gaseous-phase and aqueous-phase concentrations are stored in the separate vectors CGAS(IGAS), IGAS=1, ..., NGAS and CAQ(IAQ), IAQ=1, ..., NAQ, respectively, where NGAS and NAQ are the total numbers of gaseous-phase and aqueous-phase species.

Table 2
Nomenclature for Aqueous-Phase and Gaseous-Phase Concentrations

Quantity	Text Nomenclature	Code Nomenclature	Units
concentration of gaseous-phase pollutant	c_{gas}	CGAS	moles/cm^3 space
concentration of aqueous-phase pollutant	c_{aq}	CAQ	moles/cm^3 water
concentration of air molecules	c_{air}	CAIR	moles/cm^3 space
aqueous-phase species index	--	IAQ	---
gaseous-phase species index	--	IGAS	---

The above bookkeeping arrangement is helpful in maintaining unambiguous operations within the code, but can lead to confusion unless understood clearly at an early point in this discussion. In the example

application given in the user's manual, phosgene is scavenged by dissolution in water as follows:

$$\text{phosgene}_{\text{gas-phase}} \rightleftharpoons \text{phosgene}_{\text{aqueous phase}}$$

This leads to the two phosgene concentrations in the code,

CGAS(IGAS) ; IGAS=1

and CAQ(IAQ) ; IAQ=1

which pertain to the gaseous-phase and aqueous-phase values, respectively.

The basic governing equation describing the aqueous-phase concentration response of pollutant in a falling drop is derived from (4)

$$\begin{pmatrix}\text{Interfacial flux of pollutant away from an individual raindrop}\end{pmatrix} = \frac{K_y}{c_{air}}\left(c_{gas} - \frac{c_{aq}}{\alpha}\right) \qquad (1)$$

where the solubility coefficient, α, is defined by

$$\alpha = \frac{c_{aq}}{c_{gas}} \text{ at equilibrium} \qquad (2)$$

For the case of spherical falling drops, and recognizing that

$$\frac{dc_{aq}}{dz} = \frac{1}{v_t}\frac{dc_{aq}}{dt} \quad , \qquad (3)$$

$$\frac{dc_{aq}}{dz} = \frac{3K_y}{av_t\, c_{air}}\left(c_{gas} - \frac{c_{aq}}{\alpha}\right) + \frac{r}{v_t} \qquad (4)$$

where

a = drop radius, cm

c_{air} = concentration of air, moles air/cc space

c_{aq} = concentration of a chosen, specific chemical species in the drop, moles/cc condensed water

c_{gas} = gaseous-phase concentration of specific chemical species in air corresponding to the chosen species in the drop, moles/cc space

K_y = overall mass-transfer coefficient appropriate to the gaseous-phase and aqueous-phase substances noted above, moles/cm^2 sec

α = solubility parameter, dimensionless concentration ratio

r = chemical reaction rate of the aqueous-phase substance (moles/cm^3 condensed water)/sec (positive for generation)

v_t = raindrop fall velocity, cm/sec (negative for drops moving downward)

z = vertical position, cm

Owing to the nature of the numerical solution technique employed by this code, it is convenient to revise the form of equation (4). To accomplish this we separate the reaction into generation and decay terms as follows:

$$r = r_{gen} - r_{decay} \qquad (5)$$
$$= r_{gen} - \xi\, c_{aq}$$

where ξ is a psuedofirst-order decay coefficient for the aqueous-phase substance. We also define an inverse distance parameter $z_{inv} = z_{top}-z-z_{ground}$. Upon combination with equation (4) one obtains the form

$$\frac{d\, c_{aq}}{dz_{inv}} = \hat{C} - \hat{D} \tag{6}$$

where

$$\hat{C} \equiv \frac{-3K_y\, c_{gas}}{av_t\, c_{air}} - \frac{r_{gen}}{v_t} \quad , \tag{7}$$

and

$$\hat{D} \equiv \left(\frac{-3K_y}{av_t\ c_{air}\ \alpha} - \frac{\xi}{v_t} \right) c_{aq} \ ; \tag{8}$$

or $$\hat{C} \equiv \beta c_{gas} + \delta \tag{9}$$

and $$\hat{D} \equiv \left(\gamma + \varepsilon \right) c_{aq} \tag{10}$$

where

$$\beta = \frac{-3K_y}{av_t c_{air}} \qquad \delta = \frac{-r_{gen}}{v_t}$$

$$\gamma = \frac{\beta}{\alpha} \qquad \varepsilon = \frac{-\xi}{v_t} \quad . \tag{11}$$

Equations (6), (9), and (10) are utilized directly in code operations and will be referred to repeatedly in the following text.

Equations (1) through (4) can be applied for plumes containing aerosols and/or gases, although for particulate matter some minor mathematical manipulation is usually required. The overall mass transfer coefficient K_y can be estimated for gases using the form (5)

$$K_y = \frac{1}{1/k_y + \dfrac{c_w}{c_{air}\ \alpha k_x}} \tag{12}$$

where

k_y, k_x = individual gas- and liquid-side mass-transfer coefficients moles/cm^2 sec,

and c_w = concentration of condensed water, moles/cm^3 ($\cong$ 1/18).

k_y can be estimated using the Froessling equation (5)

$$\frac{k_y a}{D_{ay} c_{air}} = 1 + .3\left(\frac{2av_t}{\nu}\right)^{1/2} \left(\frac{\nu}{D_{ay}}\right)^{1/3} \qquad (13)$$

where D_{ay} = molecular diffusivity of pollutant in air, cm^2/sec,
D_{ax} = molecular diffusivity of pollutant in water, cm^{2}sec, and
ν = kinematic viscosity of air, cm^2/sec.

The value of k_x depends in a complex fashion on circulations within the raindrop and exposure history. For a <u>noncirculating drop</u> k_x may be estimated (4) by

$$k_x = \frac{5D_{ax}c_w}{a} \quad . \qquad (14)$$

On the basis of empirical results from experiments involving drops suspended in gas streams, it is acceptable to account for raindrop circulation by multiplying equation (14) by 2.5.(5)

In the case of aerosol scavenging it is the usual practice to set $\alpha = \infty$ in equation (4), and utilize collection efficiency values to estimate K_y. The relationship between collection efficiency and K_y (6) is

$$K_y = -\frac{1}{4} c_{air} v_t E(a) \qquad (15)$$

Equation (15) could be used in conjunction with below cloud gas scavenging calculations to account for rain scavenging of pollutant

gas-saturated cloud droplets (i.e., the plume encountering a fog). Methods for estimating the efficiency (7) are given elsewhere.

The mass-transfer discussion above suggests three options for incorporating mass transfer coefficients in gas scavenging equations. The options, and the equations utilized in subsequent model examples, are:

- Gas-phase controlled (well-mixed drop); $K_y=k_y$, and Equation (13),
- Stagnant drop; Equations (12-14),
- Intermediate; Equations (12-13) and Equation (14) x 2.5.

The MPADD code allows for input of user-specified rain spectra, which may be specific experimentally-measured values or mathematical generalizations. In either case the means for discretization is the same.

Consider the probability-density function for raindrops of radius a being collected in a bucket during some time increment Δt. A typical curve for such a function is shown in Figure 2, where N_T is the total number of drops collected in time Δt and

$$N(r_1,r_2) = N_T \int_{r_1}^{r_2} f(r)\, dr \qquad (16)$$

is number of collected drops in the size range between r_1 and r_2.

The distribution in Figure 2 can be discretized with the aid of equation (16). Select a number of consecutive size ranges $0\text{-}r_1$, $r_1\text{-}r_2$, . . ., $a_{n-1}\text{-}r_n$, where Δr_1, Δr_2, . . ., Δr_n denote the lengths of these increments. Now denote characteristic radii a_1,

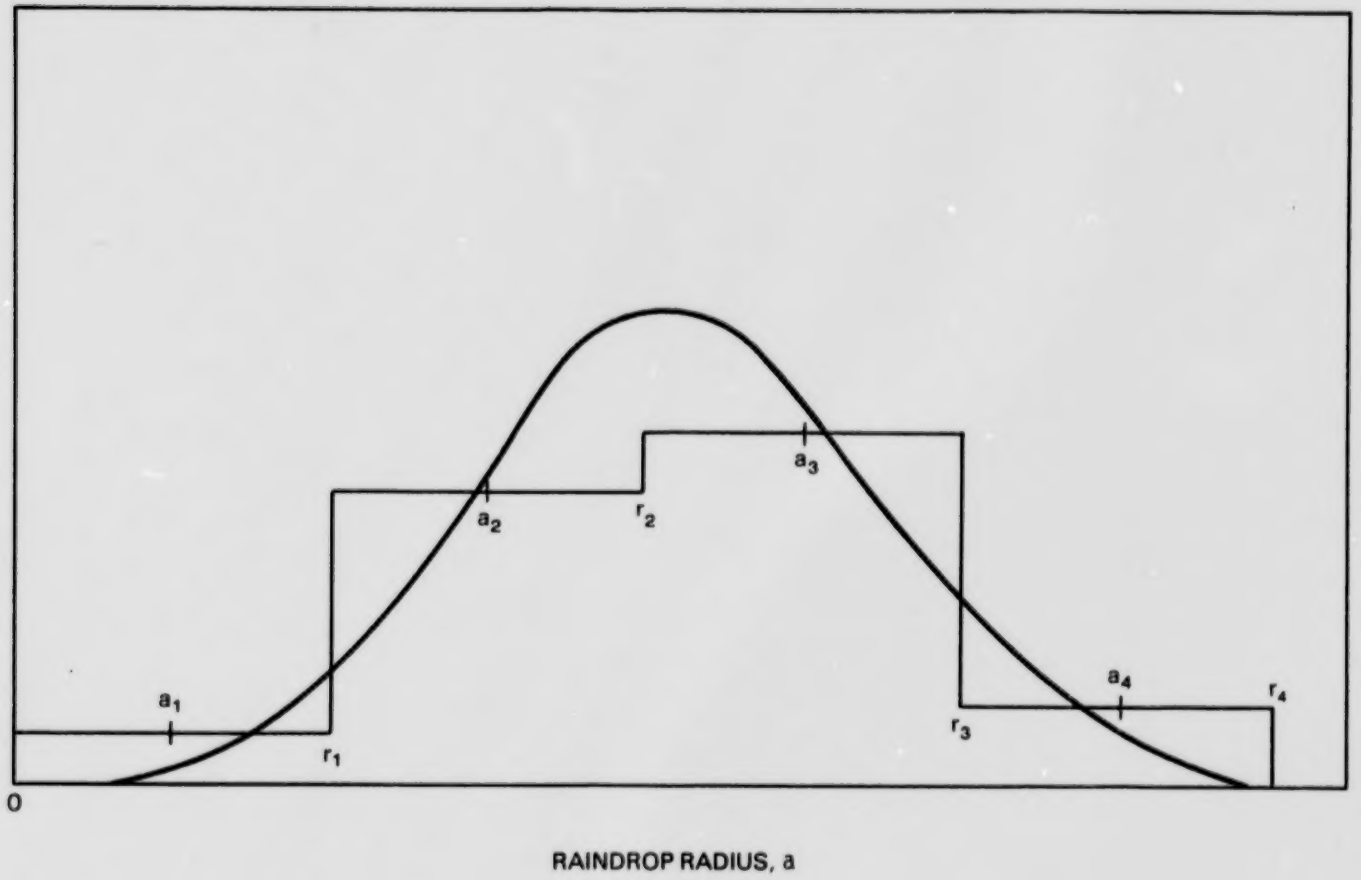

Figure 2. Continuous and discretized probability-density functions for spectrum of collected raindrops (hypothetical).

$a_2, \ldots, a_n$ as $0.5\Delta r_1$, $r_1+0.5\Delta r_2, \ldots, r_{n-1} + 0.5\Delta r_n$, giving the discretized approximation shown.

This is the interpretation of discretized spectra utilized by the MPADD code. The code's nomenclature for the normalized values of $N(r_{i-1},r_i)$ is WF(IDROP), where IDROP is the index corresponding to drop size a_i = A(IDROP). The total number of size classes in the computed raindrop spectrum is controlled by the variable NDROP, which is entered as input data.

APPLICATION FOR HAZARDOUS AIR POLLUTANTS

The MPADD model is generally applicable to problems of precipitation scavenging of any pollutant whose mass-transfer properties can be described. The pollutants of concern here (Table 1) are primarily gaseous at normal ambient conditions, and - in the absence of any contrary information (cf. Section 4 on solubility) - their solubilities (the parameter α in equation (1)) is linear, a function of temperature only. In this section, we will consider examples of scavenging of such "simple" gases, demonstrating the input data requirements, subroutines used, and calculational options. This will introduce the more specific cases of the HAP field experiments, discussed in Section 5. The User's Manual for MPADD contains an example of the reactive HAP phosgene and its treatment.

The case to be demonstrated is a ground-level area release in the manner of Figure 1, with the material of concern nitrobenzene. The subroutines that need to be made specific to this case and the corresponding input are listed in Table 3. Additional input includes the number of gas- and liquid-phase species (1 each here), the number of downwind increments and the spacing between each, and the atmospheric pressure. The virtual source point distance XUPW is the distance, upwind

TABLE 3. Subroutine Specifics and Input Data for HAP Deposition Test Case

Plume Model (PLUME)	Mathematical Form	Gaussian
	Source Height	Ground-Level (H=0)
	Spread Parameters	σ_y and σ_z (Pasquill D) (9)
	Wind Speed	U=5 m/sec
	Virtual Point Source Distance	XUPW=100 m
	Dry Deposition Velocity	Variable
	Source Term	Q=1 mole/sec
	Y-Spacing of Calculation Points	DY=0.4 (σ_y)
Raindrop Size Spectrum (RAIN)	Mathematical Form	Marshall-Palmer (10)
	Rainfall Rate	J=1 mm/hr
	Number of Size Categories	NDROP=10

(continued)

TABLE 3 (continued)

Subroutine	Required	This Example
Physical Properties (PHYSCL)	Form for β,γ	Equations (7)-(10)
	Temperature	T=278 K
	Diffusion Coefficients	D_{ay} = 0.076 cm^2/sec
		D_{ax} = 8.9 x 10^{-6} cm^2/sec
	Mass Transfer Coefficients	Regular-Equations (12), (13) and (14) x 2.5
		Stagnant Drop-Equations (12), (13) and (14)
		Gas-Phase Controlled
		$K_y=k_y$, Equation (13)
	Form for Solubility	See Figure 8
Chemical Properties	Form for δ and ε	δ,ε=0 (no reactions)

of the downwind edge of the source area, at which the source is approximated by a point. This parameter is used only in calculating σ_y, the plume spread in the y direction, thus simulating a broader plume at any positive x than what would be if XUPW=0. The form for the solubility of nitrobenzene is derived from present measurements, described in Section 4.

Diffusion coefficients are obtained from theoretical expressions, measurements at specific temperatures, and temperature-derived dependency expressions using the methods in Reid and Sherwood (8). The quantities of output of the model are listed in Table 4, and Figures 3 to 6 show results for the present example. Cross-plume concentrations are shown at a downwind distance of 500 m in Figure 3. The three mass-transfer options are shown: gas-phase controlled, where $K_y=k_y$ (equation (12-13)); stagnant drop (equations (12-14)); and the regular "intermediate" form, (equations (12-14) with k_x multiplied by 2.5). Centerline concentrations, cross-plume integrated wet flux W, and depletion Q/Q_o are shown in Figures 4 to 6 for various choices of deposition velocity V_d.

This example, employing a relatively high solubility hazardous pollutant from the Table 1 list, shows that precipitation scavenging is not an efficient mechanism for removal. It should be noted that the wet flux, and thus the cross-plume wet flux and depletion are proportional to rainfall rate,* while the dry deposition flux of course is not. Nevertheless, if a significant dry deposition velocity is appropriate (in this case $V_d \gtrsim 0.01$ cm/sec), dry deposition can outweigh wet deposition

---

*Concentration is not a function of rainfall rate, except through the weak dependence of the raindrop size spectrum.

TABLE 4. MPADD Model Output

Precipitation Features	Rainfall Rate	cm/sec
	Raindrop Size Intervals:	
	Radii	cm
	Fall speeds	cm/sec
	Volumes	cm^3
	Flux-densities	dimension-less
Concentrations ($moles/cm^3$)	In Rain (X,Y,Z)	
	In Air (X,Y,Z)	
Fluxes ($moles/cm^2 sec$)	WET (X,Y,Z)	
	DRY (X,Y,Z)	
Cross-Plume Integrated Fluxes ($moles/cm^2 sec$)	WET (X)	
	DRY (X)	
Depletion (moles/sec)	WET (X)	
	DRY (X)	

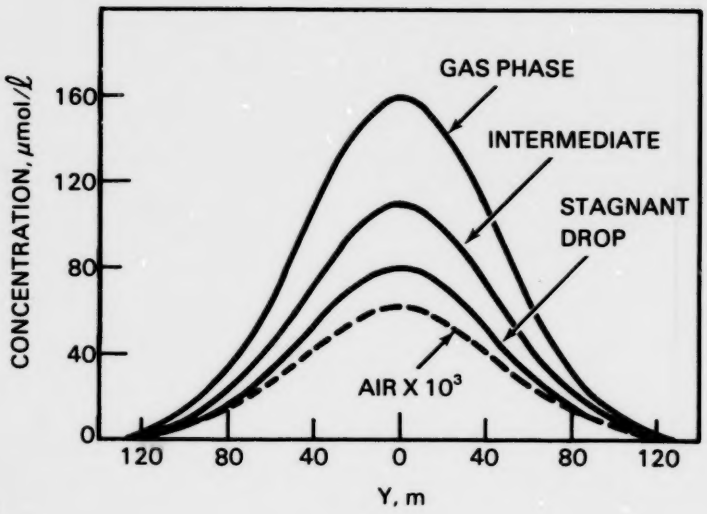

Figure 3. Concentrations vs. crossplume distance at X = 500 m. Input data for run · in Table 3.

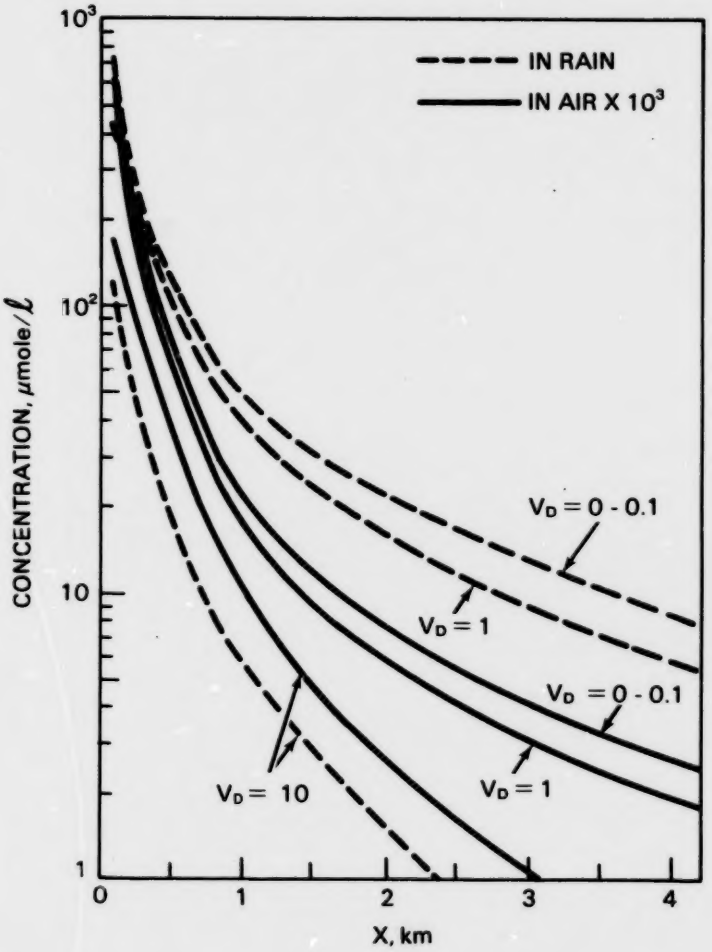

Figure 4. Centerline rain and air concentrations vs. downwind distance for various deposition velocities. Input data are listed in Table 3.

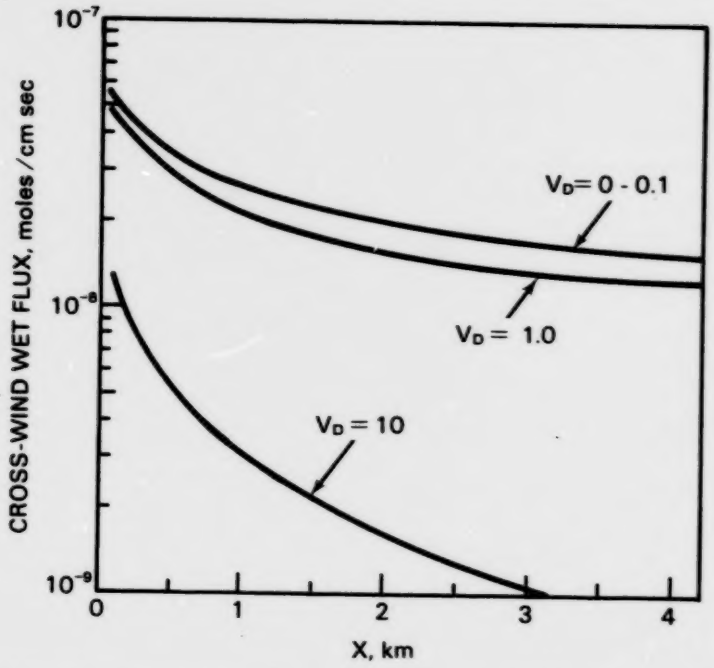

Figure 5. Same as Figure 4, but for cross-wind wet flux.

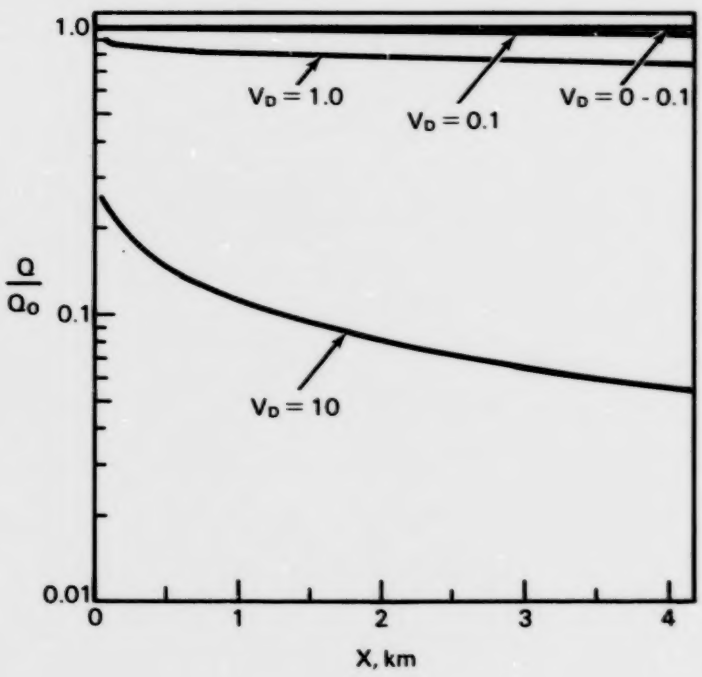

Figure 6. Same as Figure 4, but for plume depletion

for moderate rainfall rates. Wet depletion in this case is not significant (Q/Q_0>.990) out to 4 km.

It appears then, that wet deposition could be considered a minor influence on air concentrations of even relatively high solubility species from the list. At distances beyond a few kilometers (or several source heights), the liquid-phase pollutant gas concentration will be at equilibrium with the local air concentration, but a simple calculation can show that only a small fraction of the atmospheric burden will be in the liquid phase. It should be emphasized, however, that the above conclusions may not apply in cases where the pollutant is significantly reactive; conversion of the HAP by reaction may then be a non-ignorable process affecting the atmospheric concentration. Of course, the reaction products may be of some environmental concern.

It should be noted that the dry flux and depletion is quite sensitive to source height. In the present example, H was set arbitrarily to a value of 10 cm, since H=0 does not allow calculation of the maximum ground level concentration required by the dry deposition subroutine. (The maximum ground level concentration for a ground-level source is at the source point - and for a Gaussian plume its magnitude would be infinite). As a result, the dry flux and thus depletion of the plume is considerable at the first calculation distance of 100 m. Choices of lower or higher "false" source heights would give corresponding lower or higher initial deposition, but the general trend with distance beyond the first calculation point would be the same.

The figures demonstrate various ways that MPADD may be used for input to models describing the fate of hazardous air pollutants following deposition. At particular points in space, the primary output are

concentrations, and via the rainfall rate and deposition velocity, the fluxes. All input data listed in Table 3 should be considered in an application. Assuming that the forms of the subroutines of the model are set, the primary input are: source description (H, XUPW, Q), wind speed, temperature, rainfall rate and deposition velocity. Deposition velocity may be easily introduced as a function of downwind distance x; e.g., for cases of varying surface deposition characteristics. Rainfall rate may set to zero with only minor changes to the model, so that simply described downwind regions with no rain may be accounted for. More complicated descriptions of space in terms of varying rainfall rate and deposition velocity would probably require a grid system for calculation, where the spatially varying quantities would be assigned at particular points for computation.

Overall assessments of deposition can be obtained more simply by considering cross-plume integrated output and, for application to ground models, developing functions of these with downwind distance. Relevant here are the cross-plume integrated flux W(X) and depletion $Q(X)/Q_o$. An additional useful quantity might be a fractional removal rate ("scavenging coefficient")

$$k(X) = \frac{W(X)U}{Q'} \quad , \qquad (17)$$

where $Q' = Q(X)$ or Q_o, depending on the application. It should be recognized that k depends on x (whereas k is assumed to be constant in most uses of this type of parameter), and obviously k also varies with the other input parameters noted above. The potential user should be advised that particular applications should include sensitivity studies

involving important input parameters. This could result in considerable savings in computation time, if the output is found to be relatively invariant with small changes in certain input.

An important variant on MPADD is obtained utilizing an analytical solution to equation (4) under the following assumptions:

1) steady state conditions
2) negligible chemical reactions
3) wet removal may be ignored in calculation of plume concentrations (except through stepwise depletion)
4) raindrops fall through vertical trajectories.

This linear model (11) is eminently applicable to simple gas scavenging like that of the nitrobenzene example. The only significant effect of using this means of calculation follows from condition 4) above, which results in an inaccuracy close to the source point. In the example above, the linear model and the numerical integration MPADD model compare favorably for downwind distance $X \gtrsim 1$ km. For elevated sources, the agreement improves near the source.

SECTION 4

HAP SOLUBILITY

A review of the available literature concerning aqueous solubility of the compounds listed in Table 1 was undertaken to determine if there was a need for additional measurements under the present project. The review was limited to sources reporting experimental measurements of solubility parameters - normally Henry's Law constants - or calculations based on vapor pressure data. An extensive study could be performed, where all types of relevant data were assessed and further calculations made, but this was deemed beyond the scope of the solubility subobjective noted in Section 1. The results of the literature study are listed in Table 5; included are measurements made during the present project, which are discussed below. The solubilities are listed as the dimensionless parameter α, defined in Section 3. This is related to Henry's Law constant H (in units volume · pressure/mole) by

$$\alpha = RT/H, \tag{18}$$

where T is temperature (K), and R is the gas constant (0.082054 ℓ atm/K mole).

Generally, few measurements of Henry's Law constant were found, and particularly few at temperatures of atmospheric interest. An initial survey of the literature revealed that the species with the fewest experimental results available were acetaldehyde, acrylonitrile, ethylene oxide, and phosgene. Thus, these were considered for measurements along

TABLE 5. Solubility Parameters α for Hazardous Air Pollutants

Species	T, ^{0}K	α, dimensionless[a] Calculated	Measured	References
Acetaldehyde	298	>>1		(12)
Acrylonitrile	298	9×10^3		(12)
Carbon tetrachloride	293	1.04		
	298	0.86	0.81,.87	(13,14)
Chloroform	293	8.35		(15)
	298	7.57	7.21	(12)
Cresols				
p-cresol	298		2.8×10^3	(12)
4-6, dinitro-o-cresol	298		1.7×10^4	(12)
Epichlorohydrin	298	760		(12)
Ethylene oxide	278		3.8	(b)
	283	5.3		(16)
	288		6.2	(b)
	293	7.9		(16)
	303	11.2		(16)
Methyl chloroform	280		4.7	(b)
	288		2.4	(b)
	293	6.28		(15,17)
	298	5.99	4.97	(12)
Methylene chloride	298	1.5,8.04,9.1	1.4,7.67,10	(18,12,14)
Nitrobenzene	280		3.8×10^3	(b)
	288		1.7×10^3	(b)
	293	1.88×10^3		(17)
	298	1.06×10^3		(12)
Perchloroethylene	293	1.18		(15)
	298	0.85,2.4	0.85,2.0	(12,18)
Phenol	293	3.4×10^4		(19,20)
	298		1.88×10^4	(12)
Phosgene	278	4.06		(21)

(Table 5 - continued)

Species	T, °K	α, dimensionless[a] Calculated	α, dimensionless[a] Measured	References
Polychlorinated biphenyls				
Arochlor 1242	298		42.9	(22)
Arochlor 1248	298		6.99	(22)
Arochlor 1254	298		8.73	(22)
Stovhlot 1260	298		34.4	(22)

[a] Ratio of aqueous phase concentration to gas-phase concentration, see Equation (4).

[b] Present project.

with the species to be chosen for field scavenging experiments, if necessary for interpretation of the latter results. Ethylene oxide was the first choice for measurements. The remaining measurements were confined to the species used during field scavenging experiments: nitrobenzene and methyl chloroform.

The solubility cell shown in Figure 7, charged with 1000-2000 ml of a rainwater sample, was maintained at the desired temperature by circulation of cooling water from a thermostatically controlled water bath through the outer jacket of the cell (Modified Wheaton jacketed Celstir Suspension Culture Flask). The system was constructed so that aqueous and vapor samples contacted only glass or Teflon surfaces. Aliquots of a bulk rainwater sample collected at Argonne National Laboratory were used for all experiments to provide solubility data for a real precipitation sample. The composition of this sample is recorded in Table 6. A stock solution of the subject material was added

Table 6. Composition of Argonne National Laboratory Precipitation Sample Used for Solubility Measurements

pH = 4.64		NH_4^+	= 78 μmol/ℓ
$SO_4^=$	= 42 μmol/ℓ	Na^+	= 7.5 "
NO_3^-	= 40 "	K^+	= 28 "
Cl^-	= 17 "	Ca^{++}	= 23 "
Mg^{++}	= 11 "		

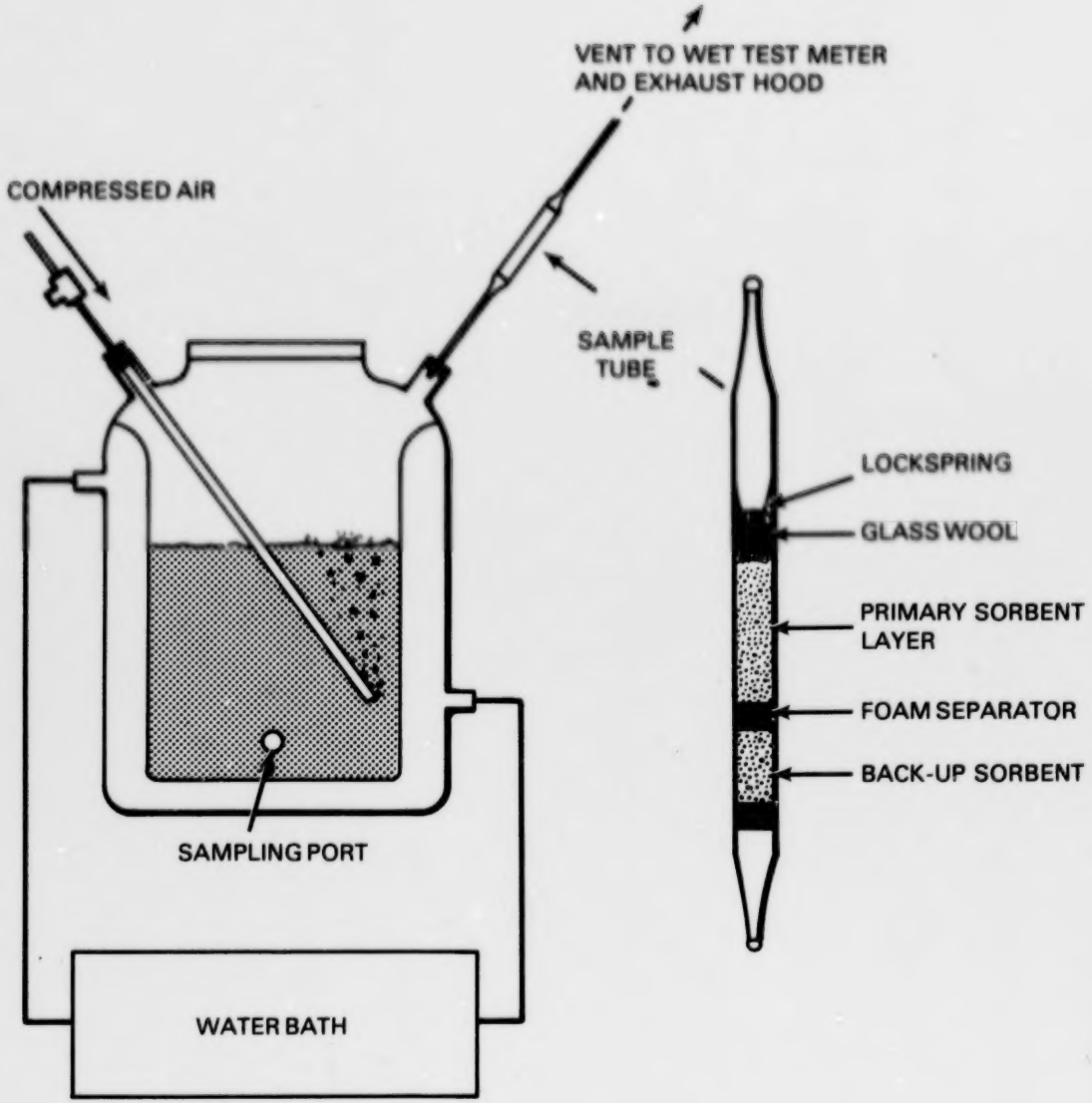

Figure 7. Apparatus used for HAP solubility measurements.

to the rainwater by removing the lid of the cell and using an all glass syringe to introduce it below the water surface. Gas flow (50-100 cc/min) was initiated and the system allowed to equilibrate by purging the vessel head space before sample collection.

The vapor in the exit stream of purge gas was collected using adsorption tubes. The mass of material collected was determined by solvent extraction followed by gas chromatographic analysis of the extract. Collection efficiencies were appraised by separate analysis of the primary and back-up sorbent layers and runs with collection efficiencies of less than 90% were discarded. Information relevant to HAP vapor collection is summarized in Table 7.

Gas flow through the adsorption tube was measured using a wet test meter or a soap bubble flow meter and the integrated vapor concentration calculated from the mass of material collected and the gas volume passed through the trap. The concentration of material in the aqueous sample was determined before and after vapor collection. Samples were taken from the vessel by syringe withdrawal through the Teflon coated septum at the sampling port.

In the case of ethylene oxide, analysis was conducted by direct GC injection of the aqueous sample.* Although the ethylene oxide peak was distorted when 1.0 μℓ samples were injected, reducing sample volume to 0.6 μℓ provided improved peak geometry and excellent reproducibility (±5%) as demonstrated by replicate analyses.

For nitrobenzene and methyl chloroform, the rainwater concentration was determined by solvent extraction. During syringe withdrawal of these

* 0.8% THEED on 80/100 Carbopak C, 91 cm x 2 mm ID glass, column temperature 40C, 20 cm^3/min N_2 carrier, flame ionization detector.

Table 7. Basic Features of HAP Vapor Collection During Solubility Runs

HAP	Adsorbent Tube	Extracting Solvent	Mass of HAP (primary sorbent) / Total Mass of HAP Collected
Ethylene Oxide	Activated Coconut Charcoal Adsorbent (Supelco 2-0267)	Carbon disulfide	>0.85
Methyl Chloroform	Activated Coconut Charcoal Adsorbent (Supelco 2-0267)	Pentane	>0.98
Nitrobenzene	Silica Gel Sorbent Tube (SKC #226-10)	Methanol	>0.89

materials special care was taken to avoid the introduction of air from around the barrel of the syringe. One milliliter of this sample was transferred to a mini-reaction vial containing a measured volume of the extracting solvent and the transfer conducted below the surface of the solvent. Samples were generally analyzed within 30 minutes of collection and concentrations quantified by peak area using a Hewlett-Packard Model 3380A integrating recorder, calibrated using a multipoint external calibration method.

Calculated HAP solubilities, expressed as the dimensionless Henry's Law constant α (aqueous concentration/air concentration) are recorded in Table 8. These values, which are generally the average of three separate solubility runs, have been derived from the corresponding average water and air concentrations. The errors associated with various measurements contributing to the solubility expression are expected to introduce an uncertainty of ±10% in the values reported for nitrobenzene and ethylene oxide and ±15% for methyl chloroform.

Table 8. HAP Solubility in Rainwater

Compound	α, Dimensionless	Temp, C
Ethylene Oxide	3.4×10^2 ±0.3	5
	2.0×10^2 ±0.2	15
Methyl Chloroform	2.4 ± 0.4	15
	4.7 ± 0.7	7
Nitrobenzene	3.8×10^3 ±0.4	7
	1.7×10^3 ±0.2	15

The nitrobenzene data are in good agreement with the previous measurements, but the methyl chloroform values are generally lower than the temperature trend expected from the data previously reported (cf Table 5). The present measured solubilities were used to produce temperature functions of α for applications of the deposition model MPADD in Section 3 and in Section 5.

SECTION 5

FIELD EXPERIMENTS

The major experimental task of the project was the performance of controlled-release field experiments. While the solubility survey and measurements provided perhaps the most important scavenging-related input to the atmospheric deposition model MPADD, actual field measurements were highly desirable to provide a data base for testing the output, namely estimates of rainwater concentrations and deposition patterns. In this section we discuss the design and conduct of the experiments, the experimental results and comparisons with MPADD model calculations.

EXPERIMENT DESIGN

The major consideration in the design of field experiments to test precipitation scavenging models is the choice of pollutant source. The two basic types of source are: preexisting, consisting of known input of pollutant to the atmosphere; and controlled-release, contrived especially for the purposes of the measurements. In the case of potentially hazardous air pollutants, examples of the former include industrial point or area sources, hazardous waste dumps, and transportation or industrial spills. The major advantage of preexisting sources is that the pollutant is already present in the atmosphere, and the experimenter's safety considerations only involve sampling and analysis, and not justifying the impact of contributing to the atmospheric burden of the pollutant. In addition, the test cases are real, of the sort that the scavenging model is intended to treat.

There are many disadvantages, however. The source configuration may be poorly characterized, and emissions may be variable and discontinuous. Potential logistical problems include sampling in problem terrain, identification and quantification of the true source of measured pollutants, and the necessity to wait in the field for the proper conditions. The latter is a particularly severe constraint when the budget is limited, and success or failure of the project may be greatly due to chance.

Advantages of controlled-release experiments include: more precise control of source configuration and release rate (and resulting relative simplicity of the model simulation), and the ability to chose when and where to conduct the measurements. The major disadvantage is that the releases must be conducted safely and in the interest of public health.

We chose to perform the experiments in a controlled-release manner, primarily because of budget constraints, and because (as is shown below) an experimental location within the Hanford Site was particularly advantageous in terms of safety and logistics.

The conceptual design of the experiment is similar to the generalized concept of the MPADD model shown earlier in Figure 1. An elevated source point was selected to minimize dry deposition of the pollutant plume upwind of the sampling locations. Since most of the HAP's under consideration for release are liquid under normal conditions, the elevated source also provides leeway for volatilization of the plume prior to sampling. The Hanford meteorology tower was used as the source location, and sampling was performed on pre-existing arcs of the Hanford diffusion grid. The source height (26 m) and the

sampling distances (200 and 400 m) were chosen as a compromise between the desire for low dry deposition (high source and close sampling) and the need for complete volatilization (distant sampling) and avoidance of undercutting of the plume by collected raindrops (low source).

The Hanford diffusion grid is located near the center of the 1480 km^2 Hanford Site, administered by the U.S. Department of Energy (DOE). As such, the area access is under strict control, and releases of HAPs could be performed safely. Plume model estimates of ground-level air concentrations resulting from the desired release rates for specific HAPs showed that under experimental conditions, exposure levels above 8-hour average guidelines would not occur in the experimental area.

Adjacent to the experimental area is the Hanford meteorology station, which is a 24-hour forecast center for the Hanford project. The experienced forecasters at this station have access to all data needed for forecasting of precipitation events. Therefore, although rainfall is infrequent and generally light at this desert location, the prognosis for successful completion of several experiments during the early months of 1983 was good.

HAP Release Mechanism

Considerations of safety were of major importance in the design of the mechanism for release of the HAP. Although under experimental conditions control of the releases could be obtained safely by a properly-attired operator, accidental spills or ignition of the material could not be ruled out. Thus, the release point on the tower could not

be manned during the experiments, and remote monitoring and control was necessary. Aside from safety, the main requirement of the mechanism was that it disperse the liquid HAP's in a fine mist such that volatilization of the plume would take place quickly before a significant amount of the material would be scavenged as droplets. This consideration dictated that the HAP be sprayed under pressure through efficient ultrasonic nozzles, and that the material should either be highly volatile itself or carried by a high-volatility carrier solvent.

Figure 8 shows the generation and control centers utilized for the experiments. The dispenser is a 25 cm diameter aluminum tube fitted with two Sonicore 86H ultrasonic nozzles. A fan at the back end of the tube provides an air flow always toward the release end while the system is turned on. In addition, 5 to 10 cfm (140-280 ℓ/min) of "sheath" air is directed forward from a ring just behind the nozzles, to enhance the air flow direction and provide turbulence for the nozzle spray. Large ring heaters on the dispenser tube warm the sheath air and the general neighborhood of the spray. High pressure air and tracer liquid are provided to each nozzle separately, and sensors monitor the air temperature at two points inside the dispenser. The pressure tank, which was heated and temperature-controlled to about 30 C, has a capacity of 35 ℓ. It was pressurized just enough to provide smooth flow of liquid to the dispenser under the standard operating conditions of the nozzles. The valve box and display panel contains regulators and valves for all air supplies and remotely controlled valves for sheath air, tank pressure, and liquid flow. Flow rates, pressures, and temperatures (including of the liquid in the tank) were displayed to a TV camera. Once the equipment was connected, air supplies turned on,

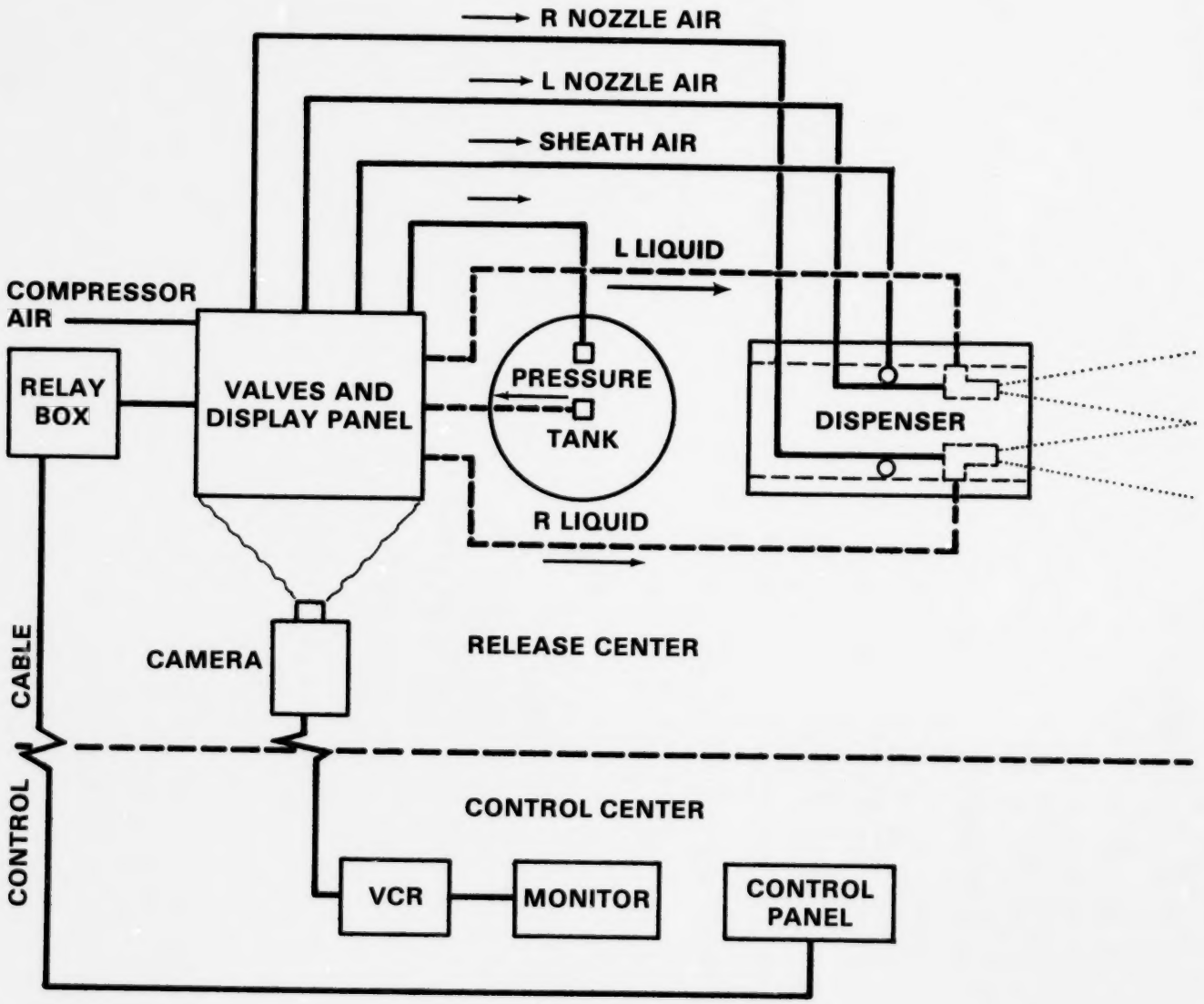

Figure 8. Schematic of HAP generation and control systems

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and the camera set up, all control of the functions was done from the control center on the ground about 50 m from the tower base.

Testing of the release apparatus using non-hazardous solvents (methanol and hexane) established operating settings for the releases, and visual confirmation was obtained for volatilization close to the dispenser outlet. See Appendix A for liquid flow meter calibrations. The nozzles were set to operate at about 40 psig and about 6 cfm (170ℓ/m) each. The total liquid flow range was established at ∿100-500 mℓ/min, allowing sufficient release during a one half hour release for a good chance at detectability in the sampled rain.

HAP Selection

The selection of materials to be included in the series of scavenging experiments conducted under this program was based on the following considerations:

- solubility
- analytical sensitivity
- volatility
- toxicity
- reactivity
- relative importance as industrial chemicals

Under the constraints imposed by the Hanford climatology (which typically provides only a limited number of suitable events during the window available to the experimental program), the lead time required to activate the sampling network, and the time required to prepare the laboratory to receive precipitation samples, primary emphasis was given to the selection of materials with significantly different solubilities. The initial list of candidates was therefore reduced to nitrobenzene,

methyl chloroform, and dichlorophenol. Nitrobenzene possesses the desirable characteristics of high aqueous solubility and low volatility. In contrast, methyl chloroform is representative of a large number of industrial halocarbons characterized by low solubility and high volatility. Dichlorophenol was selected as a alternative to phenol, a soluble material of relatively low volatility which is prone to biological degradation in environmental samples.

Sampling and Analytical Techniques

While aqueous solubility was the dominant consideration in the selection of HAP's for the scavenging series, volatility was also factored into the decision process and was weighed heavily in identifying the material to be utilized in the initial field experiments. The potential for loss of organic from the collected rainwater to the headspace of the collector, or to the atmosphere, was a serious consideration in design of a collector. The first identified requirement was that the collector be of the funnel-bottle type rather than an open bucket, so that diffusion of the organic vapor to the atmosphere would be minimized. However, headspace in the bottle could not be eliminated because a reasonably large area funnel was needed to collect sufficient amounts of the generally light rain; it followed that the bottle would need to be large ($\geq$500 ml) so as to not overflow if a heavy rain should occur. The resulting design is shown in Figure 9. The 10 cm diameter polyvinyl chloride (PVC) pipe, flared at the top, supports the funnel and prevents blowaway in even strong winds. The 500 ml amber glass bottle rests in the pipe cap, and the funnel rests against the flared pipe. The 22 cm diameter funnel is of Teflon-coated aluminum.

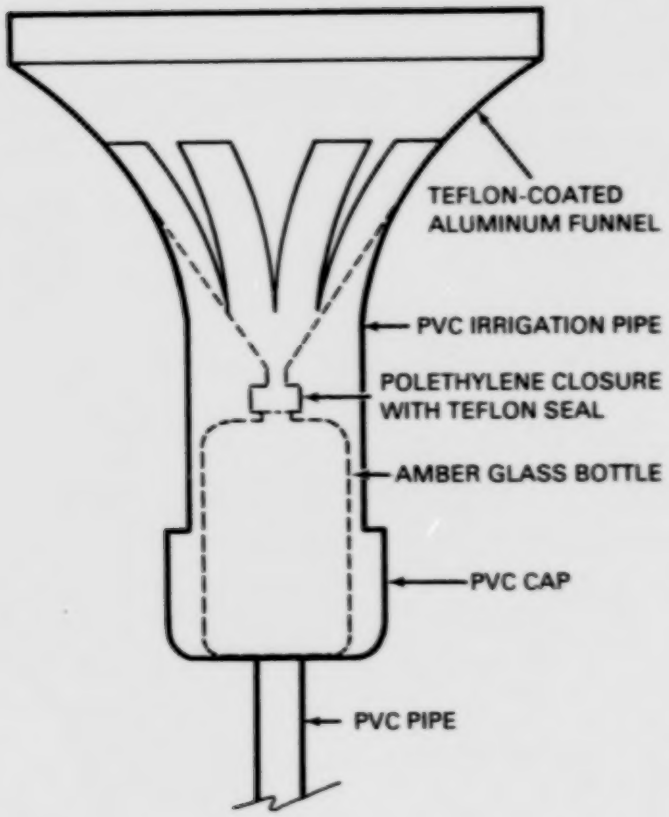

Figure 9. Schematic of bulk precipitation collector.

Although a pollutant species which would minimize the potential for volatilization between collection and analysis was selected for the initial experiments, the collection scheme anticipated subsequent experiments (i.e., using methyl chloroform) in which evaporative loss was of greater concern. This scheme incorporated the addition of an organic solvent to serve as a barrier to analyte volatilization. This approach was also consistent with the solvent extraction procedure adopted for analyte concentration and analysis. Ethylacetate was selected as the solvent to be used for initial scavenging experiments involving nitrobenzene but was found to be inefficient in concentrating this material from aqueous solutions. A 15:50 ratio of ethylacetate to water provided only 13.5 $\pm$ 0.4% analyte recovery for samples spiked with 120 to 2400 ng of nitrobenzene. As an alternative, pentane was investigated for use in the experimental series. Although it is itself volatile, pentane was found to be retained as a solvent barrier over precipitation in the collection bottle under the meteorological conditions prevailing during the late winter, early spring series. In addition, a preliminary laboratory study in which distilled water samples were spiked with nitrobenzene and 1,3-dichlorobenzene, the extraction standard to be employed in the scavenging study, demonstrated efficient pentane extraction. A summary of these findings is recorded in Table 9.

Additional tests in which spiked precipitation samples were allowed to drop slowly into the precipitation collector were conducted to assess the potential for in-field losses of nitrobenzene. The results of these tests shown in Table 10 are consistent with the retention of scavenged

TABLE 9. Pentane Extraction of 1,3 Dichlorobenzene and Nitrobenzene from Spiked Deionized Water Samples

Aqueous Concentration, ng/ml		Per Cent Recovery	
1,3 Dichlorobenzene	Nitrobenzene	1,3 Dichlorobenzene	Nitrobenzene
26	24	82	89
26	12	89	97
26	2.4	77	113
26	24	82	94
26	12	77	93
26	2.4	78	120
5.2	14.4	85	98
5.2	9.6	82	94
5.2	4.8	84	93
5.2	2.4	91	87
5.2	1.2	85	69
5.2	0.5	84	84
5.2	4.8	70	98
5.2	1.2	92	93
5.2	0.5	90	125
		83.2%	96.5%
		±6.0	±14.0

TABLE 10. Simulated Precipitation Collection Recovery of 1,3 Dichlorobenzene and Nitrobenzene from Spiked Precipitation Samples

Concentration, ng/ml		Percent Recovery	
1,3 Dichlorobenzene	Nitrobenzene	1,3 Dichlorobenzene	Nitrobenzene
--	5.2	--	98
5.2	0.5	28	94
--	1.2	--	78
5.2	0.7	24	73
--	0.2	--	142
--	0.5	--	103
--	0.7	--	97
--	1.0	--	139
--	0.2	--	115
--	0.5	--	96
--	0.7	--	93
--	1.0	--	111
--	0.2	--	108

nitrobenzene in collected precipitation. Where 1,3 dichlorobenzene was added to the precipitation sample to simulate in-field collection, significant loss was observed following dropwise transfer to the collector. More importantly, the results of tests summarized in Tables 9 and 10 demonstrate efficient recovery from aqueous solution by pentane extraction and the absence of interference with the quantitative detection of nitrobenzene and the extraction standard 1,3 dichlorobenzene in natural precipitation. Specific features of the analytical scheme developed during these tests and employed during scavenging experiments using nitrobenzene are summarized in Table 11.

While the solvent extraction technique was successfully applied during nitrobenzene experiments, the use of methylchloroform represented a particular experimental challenge. The purge and trap method is the preferred technique for analysis of volatile halo-carbons in surface waters (EPA method 601). Solvent extraction has however been reported (23-26) and is consistent with the sample collection method used earlier. Preliminary experiments focused on pentane as the extracting solvent and were conducted to both document a procedure for sample work-up and establish extraction efficiency.

Coincident with this work, the performance of various GC columns and the sensitivity of the electron capture detector(ECD) was investigated. Of particular concern in the selection of a GC column was the separation of methylchloroform and carbon tetrachloride peaks. The reported use of carbon tetrachloride at Hanford suggested its possible presence in collected precipitation. Two columns were demonstrated to

TABLE 11. Summary of Sample Collector Preparation and Precipitation Work-up Procedures for Nitrobenzene

- Pre-deployment Procedures

1) Wash amber bottles in soapy water, rinse with distilled deionized water and dry at 100C.

2) Add ∿30 ml of pentane to the collection bottle before transport to the collection site.

- Sample Retrieval, Work-up and Analysis

3) Seal collection bottle with Teflon lined cap.

4) Add 260 ng of 1,3-dichlorobenzene to water layer.

5) Shake water-pentane mixture and transfer to clean separatory funnel (10-15 ml of pentane was generally left at the end of a scavenging experiment).

6) Rinse collection bottle twice with ∿5 ml of pentane and add the rinse to the mixture in the separatory funnel.

7) Conduct separation, the aqueous layer is returned to the amber collection bottle and the pentane extract is transferred to a 11 dram vial. Rinse separatory funnel with 10 ml pentane and add to extract.

8) The pentane extract is evaporated slowly under a stream of clean prepurified He to reduce the volume to ∿5 ml.

9) Samples are stored at 4C before G.C. analysis using a HP model 5736 gas chromatograph with electron capture detector, 1.8m x .32 cm OD (6 ft. x 1/8 in.) SS 10% OV-17 on 80/100 Supelcoport W HP N_2 carrier, 20 cm^3/min.

provide good separation of these materials.* While pentane remaining from the nitrobenzene experiments was used to evaluate GC performance, a set-back was encountered when a fresh pentane sample intended for use in the extraction tests was found to contain significant levels (2.6 ng/ml) of methylchloroform and other low molecular weight halocarbons. Although a quantitative evaluation of the extraction of methylchloroform at low concentration levels in spiked precipitation samples was not possible, experiments were conducted with samples containing 300-500 ng of methylchloroform to provide a qualitative indication of analyte recovery using a sample work-up procedure similar to that applied to nitrobenzene. This work suggested a methylchloroform recovery of ~82%. The same samples, spiked with carbon tetrachloride and tetrachloroethylene, provided 68 and 69% recovery of these materials.

The question of recoverability of methyl chloroform at low levels from precipitation samples remained, however, and the conduct of a field experiment was delayed pending the arrival of high quality pentane and further analyte recovery experimentation. Since the rainy season was drawing to a close (it was now late March, 1983), it became clear that any good opportunity must be seized. Therefore, the methyl chloroform experiment was conducted before further testing could be done, although the good pentane had arrived. The analyte recovery testing was performed concurrent with the field experiment; results of this testing and a description of the analysis leading to interpretation of field experiment chemical results are described in Appendix A.

* 10% Apiezon L on 80/100 Supelcoport W HP
1.8 m x .32 cm (6 ft. x 1/8 in.) OD SS
26 cc/min carrier, 100°C column temp.

5% SE-30 on 80/100 Supelcoport W HP
1.5m x .32 cm (5 ft. x 1/8 in.) OD SS
27 cc/min carrier, 70°C column temp.

Supporting Measurements

Meteorological input data for MPADD model calculations simulating the field experiments were obtained from several sources. Mean wind and turbulence data were collected by Gill three-dimensional anemometers mounted on a tower about 1.5 km from the release point. The measurements at 7 levels (1,2,4,8,16,32,61 m) and subsequent computer analysis provided release-time averages of mean horizontal speed and direction, and standard deviations in the azimuth (σ_θ) and the vertical directions (σ_ϕ). Mean wind direction and speed, and temperatures at the 15 and 30 m levels of the Hanford meteorology towers were also recorded manually during releases. Raindrop size spectra were measured by use of calibrated water sensitive paper (27). One or more rain spectrum samples were collected during each release, and the images electronically sized later.

Rainfall rate was measured using a Belfort weighing gauge, modified to increase the collection area to 1 m^2. This rate measurement was used mainly for monitoring during releases, as the collector exposure (on the roof of the control center trailer) was not precise. The "official" rainfall rate during releases was obtained by comparing the rate obtained during run times, with the collection of rain in sampling containers exposed on the sampling arcs.

Operational Procedure

During the period of readiness for experiments, from mid-January to mid-April, 1983, the Hanford meteorological station shift forecasters advised us when it appeared that frontal rain conditions were expected in the next 24 hours. The general criteria were the anticipation of several hours rain totalling about 0.15 cm (0.05 in.). During the period following, the HAP material to be released was prepared, and

sampling and generation equipment readied. When it was determined that experiment conditions may occur within the next few hours, field personnel were sent to the site, the generation apparatus requiring pre-warming (air compressor, HAP pressure tank heaters) turned on, and the video camera activated. If time permitted, the HAP mixture was allowed to warm for several hours, then the air and liquid flow rates were set. In the case of the nitrobenzene-hexane mixture, the liquid flow rate was set using pure hexane from the auxiliary pressure tank. Due to the difference in density between hexane and the mixture, the flow rate was set slightly higher for hexane than what was desired for the mixture during the release. The methyl chloroform flow setting was done (prior to sampler set out) using the material itself. This was permitted because of the higher exposure allowances for methyl chloroform and its nonflammability. After the flows were set, the liquid flow was stopped and the generator operator left the tower. From that time until the release would begin, all equipment was left on except the sheath air and liquid flow. If a delay of several hours seemed likely, the air compressor was turned off; this would necessitate restarting and warming it prior to a release. The tank temperature was monitored during the entire period before release.

At this time, a decision on expected proper sampler locations was made on the basis of forecast advice, and sampler funnels and bottles were deployed. Meanwhile, the generator operator started the wind data recording and blocked off access to the experimental area.

When rain and wind conditions were considered acceptable (and often this followed several hours wait), and some samplers redeployed if necessary, the release was started and times noted. During the release period (ranging from 11 to 32 minutes), contact was maintained with the

meteorology station, where temperatures were recorded and wind conditions monitored, and the video screen was monitored for any signs of improper release conditions. At one or more times during the release, raindrop spot samples were collected on sensitive paper for later raindrop spectrum analysis. Normally, enough HAP was loaded for a 30 minute release, but any improper change in generation rate, wind direction or rainfall could result in an earlier termination.

After the release was terminated, approximately 20 minutes passed (to allow the release plume to clear the downwind area) before sample collection was begun. The personnel collecting the samples were careful to remove the funnels and recap the collector bottles with clean Teflon-lined caps immediately. Sample position numbers were recorded and checked. The samples were returned to the laboratory refrigerator to await analysis. Meanwhile, the wind data recording was stopped and the tape recovered.

When all samples were secured, the generator operator returned to the source point, disconnected the generator tank and flushed the generator system with solvent from the auxiliary tank. The tank containing the remaining HAP mixture was weighed for determination of mass released.

EXPERIMENTAL RESULTS

During the winter 1983 experiment period, four successful releases of HAP materials were accomplished. Runs involving nitrobenzene occurred on February 10 and 18. The first of these included two separate releases, separable as experiments because of different wind directions. A fourth experiment involving methyl chloroform took place on April 1, 1983.

General Summary of Experiments

In most field projects involving new methodology and adaptation of it to the vagaries of meteorological conditions, the first experiment of the series often suffers from difficulties, and the present run H1 is no exception. Because of the possibly hazardous nature of the material being released, it was not possible to test the release equipment with the actual mixture prior to the first scavenging experiment. Therefore, proper performance could not be ascertained until the experiment was underway. Unfortunately, an unanticipated property of the nitrobenzene-hexane mixture resulted in some confusion during the experiment, and a subsequent lowering of accuracy of vital experimental data. On the positive side, we were able to separate some of the adverse effects after the fact, and (as will be shown below) make some estimates for usable model comparisons.

The prefrontal rainfall of the evening of February 10, 1983, was very light in intensity, but the wind direction and speed were acceptable at the beginning of the release. The liquid flow rate began at about 150 mℓ/min instead of the preset and anticipated 500 mℓ/min, and slowly decreased over eleven minutes to about 100 mℓ/min (near the poorly-calibrated low end of the liquid flow meters), when it was decided to terminate the release. The reason for the low flow could not be determined exactly without dismantling the equipment and terminating the day's activity; it was assumed that there was some blockage in the liquid line from the pressure tank. Since (apparently) less than 10% of the nitrobenzene had been released, an amount which was estimated to be insufficient for detectability in collected rain samples, it was assumed that the release was a failure, but another try could be made, when perhaps the malfunction would have corrected itself.

The second release was for 21 minutes, and the flow rate was about 350 mℓ/minute, dropping only to about 300 near the end. The wind direction had changed, so that the deposition plumes (if any) from the two releases could be separated.

Subsequent to the experiment two facts were learned: both deposition plumes were measurable, and the hexane/nitrobenzene mixture separates at temperatures below about 5°C. Thus the low flow rate was due to release of a denser layer of liquid - perhaps pure nitrobenzene - at the bottom of the tank during the first release (H1-A). The second release (H1-B), several hours later after the tank had warmed and the mixture remixed by convection, appeared more normal. Thus, there were two separable experiments, but the source terms - the masses of nitrobenzene released - could only be estimated due to the unknown nature of the mixtures at the time of release. These source terms were estimated, and are discussed below and in Appendix A.

Run H-2 was performed on February 19, 1983 in the morning hours. The generation equipment and samplers had been activated at about midnight, and the nitrobenzene mixture was assured to be well mixed. Precipitation began about 0500 PST but the wind was calm. In anticipation of later winds, but of unknown direction, the samplers were deployed over a wide sector at double spacing (8°) on both arcs. The release went off normally, with expected flow rates for 29 minutes.

Run H-3 was conducted on the evening of April 1, 1983. The material was methyl chloroform, which, because of its relatively high volatility, could be released full strength. Since we faced a greater problem in analytically detecting methyl chloroform in the rain samples due to its lower solubility, essentially all available material was released over a 32 minute period.

Meteorological and Source Term Results

Table 12 presents general information and meteorological data for the field experiments. The wind speed, direction and standard deviation of the horizontal and vertical components (σ_θ and σ_ϕ, respectively) were calculated as averages over the time spans indicated for the releases. Various wind sensors were out of service during the releases; as a consequence, estimates of speed were made from an extrapolation of the logarithmic wind profile for run H-1 and H-2, and as an average of levels bracketing the source height (26m) for H-3. The wind direction and standard deviations were determined at the levels indicated in the table. The measured standard deviations were reasonable when compared with values calculated from empirical expressions for neutral (Pasquill class D) stability (9) in all cases except run H1-B. In that case, where the wind speed was very low, the wind direction variance was much larger than the values for H1-A, two hours earlier, and was apparent at all operating measurement levels. Further discussion of this observation appears in the model comparison section below. Temperature data were taken from the Hanford meteorological tower measurement at 30m height.

Rainfall rates for the runs are shown in Table 12. The rainfall rate could not be precisely measured because of the low rates, especially for run H1. A standard raingauge with a resolution of 0.25 mm (0.01 inch) is not sufficient to evaluate rates like those experienced over time spans of a half-hour or so. In anticipation of this, we modified a standard raingauge to expand the collection area to 1 m^2 (the normal area is 324 cm^2). Thus much greater rainfall resolution could be obtained. The collection efficiency of this device was not comparable (apparently) to a standard gauge, however, but it

TABLE 12. RELEASE TIMING AND METEOROLOGICAL DATA[a]

Run No.	Date	Time PST	Wind				Temperature[e] C	Rainfall Rate mm/hr
			Speed m/sec	Direction Degrees[b]	σ_θ[c] Radian	σ_ρ[d] Radian		
H1-A	2/10/83	2021-2032	2.5(26)[f]	320(4)	.12(8)	.08(8)	3.3(30)	.39
B	2/10/83	2213-2234	1.5(26)[f]	290(4)	.90(8)	.22(8)	2.2(30)	.28
H2	2/18/83	0758-0827	3.0(24)[g]	313(8)	.12(32)	.07(32)	5.3(30)	1.3
H3	4/1/83	1912-1944	2.7(24)[g]	320(24)[g]	.16(32)	.08(32)	5.8(30)	0.8

a Elevation of measurement (m) in parenthesis.
b Azimuth from true north.
c Standard deviation of horizontal wind.
d Standard deviation of vertical wind.
e Hanford meteorological tower average for hour of run.
f Extrapolated from profile determined by 1,2,4 and 8m level measurements.
g Average of values measured at 16 and 32m levels.

could be determined by comparison with a standard raingauge over a sufficiently long time span with sufficient rainfall. Unfortunately, this could not be done because the rain events experienced did not meet these criteria. The next best thing was to compare the raingauge results with rates computed from the volumes collected by the precipitation collectors on the arcs. These volumes were collected over periods much longer than the actual release times, and were quite uniform, indicating good collection properties for the collectors. Complete collection volumes are listed in Appendices A and C. Table 13 shows the results of comparing the collectors with the "fast" raingauge. The consistency of the ratio of fast raingauge volume to collector volume is fortunate - apparently the rain and wind conditions of the run days were very similar in terms of factors which affect collection efficiency. The remaining question is whether the sample collectors collection efficiency is close to that of a standard raingauge; we expect it is on the basis of considerable experience in using collectors of that shape during past field projects (28-30).

The raindrop flux density distributions (as defined in Section 3) for the runs were determined from sizings of spot images collected on calibrated treated filter papers (27), and are listed in Table 14. The raindrop spectra are very similar, and typical of frontal raindrop size spectra we have measured before in the Pacific Northwest (31). Only one usable rain size sample was collected for run H1, so it is used to serve for both parts of that run.

The source terms Q (mass of material released per unit time during the runs) are listed in Table 15. These values were determined in two ways, for quality control purposes, and also because the primary means of determining Q - liquid flow meter readings - was inaccurate due to

TABLE 13. RAINFALL RATE COMPARISONS
BETWEEN COLLECTORS AND "FAST" RAINGAUGE

	Mean Volume,[a] ml			Mean Rate,[c] mm/hr	
Run	Collectors	Fast Gauge[b]	Ratio	Fast Gauge	Corrected[d]
H1	53	36	.68		
H1-A				.27	.39
H1-B				.19	.28
H2	214	150	.70	.91	1.3
H3	76	49	.65	.52	0.8

a Over time of exposure of collectors.
b Volume in collectors expected using rate calculated from fast gauge.
c Over time of HAP releases.
d Fast Gauge/Collector Mean Ratio.

TABLE 14. RAIN SIZE DATA

Radius Interval, cm	Flux Density (Fraction in Interval) Run H1	Run H2	Run H3
0.-.015	.006	. 0	.001
.015-.030	.334	.370	.269
.030-.045	.240	.240	.310
.045-.060	.120	.205	.170
.060-.075	.135	.095	.110
.075-.090	.080	.045	.040
.090-.105	.025	.027	.040
.105-.120	.025	.009	.040
.120-.135	.015	.004	.010
.135-.∞	.020	.005	.010

TABLE 15. SOURCE TERM Q (MOLES/SEC) RESULTS

Run	Q
H1-A	0.0058 ± 60%
B	0.0058 ± 30%
H2	0.011 ± 5%
H3	0.028 ± 5%

visibility on the television monitor. The backup, and more precise measure, was through differences in weight of the pressure tank and contents before and after the releases. As described above, the source terms for runs H1-A and H1-B were uncertain due to the separation of the nitrobenzene/hexane mixture. The values of Q for these releases were estimated by a procedure which is detailed in Appendix B, which also contains complete source term data for the other runs.

Chemical Results

The measured concentrations of nitrobenzene, for runs H1 and H2, and methyl chloroform, for run H3, in rainwater are listed in Table 16 and 17. Complete sample data, including collected rain volumes, background measurements, and multiple measurements on samples are reported in Appendix A for methyl chloroform and Appendix C for nitrobenzene. The chemical analysis procedures produced masses of the released species in the rain samples; concentrations were determined by dividing these masses by the volume of rainwater predicted from the rainfall rates listed in Table 12. Because of the very light rainfall during both parts of run H1, the actual rain volume collected during the release was small; subsequently, errors from rainfall rate determination result in about a 25% uncertainty in concentration. The corresponding expected errors for H2 and H3 are ±10%.

Chemical results for methyl chloroform in rainwater for run H3 are sparse and subject to considerable uncertainty due to sample handling and contamination problems described in Appendix A. Inconclusive results were obtained from the arc A samples, whose analysis was done first. A modified analysis procedure, with careful examination of contaminating species (carbon tetrachloride and an unknown, possibly trichloroethylene) allowed determination of likely methyl chloroform

TABLE 16. OBSERVED AND CALCULATED NITROBENZENE CONCENTRATIONS, μmol/ℓ, RUN H1

RUN H1-A

	ARC A[b]			ARC B[f]		
Arc Position[a]	y-units[c]	OBS.[d]	CALC.[e]	y-units[c]	OBS.[d]	CALC.[e]
130	-3	0.092	0.18	-6	0.046	0.09
134	-2		0.46	-4	0.032	0.22
138	-1	0.15	0.83	-2	0.15	0.39
142	0		1.0	0	0.15	0.46
146	1	0.32	0.83	2	0.18	0.39
150	2		0.46	4	0.049	0.22
154	3	0.062	0.18	6	0.025	0.09
158	4		0.05	8	0.022	0.03
162	5	0.032	0.01	10		0.01
Cross-plume flux W, moles/cm sec x 10^{10}		0.21	0.61		0.20	0.58

RUN H1-B

098	-3	0.14	0.33	-6	0.13	0.17
102	-2		0.83	-4	0.34	0.40
106	-1	0.39	1.4	-2	0.63	0.68
110	0		1.7	0	1.2	0.82
114	1	0.88	1.4	2	0.43	0.68
118	2		0.83	4	0.081	0.40
122	3	0.14	0.33	6	0.043	0.17
126	4		0.09	8	0.029	0.05
130	5	0.06	0.02	10	0.033	0.01
W, moles/cm sec x 10^{10}		0.35	0.78		1.3	0.75

[a] Azimuth from true north

[b] Downwind distance 200 m

[c] y-unit ≃40m

[d] ± 25%

[e] ± 60% for H1-A, ± 30% for H1-B

[f] Downwind distance 400 m

TABLE 17. Observed and Calculated Methyl Chloroform Concentrations, Run H3, Arc B

Arc Position[a]	y-units[b]	Concentration, μmol/ℓ x 10^3 Obs.[c]	Calc.
114	-12	--	.1
118	-10	--	.3
122	- 8	0	.8
126	- 6	4.2	1.7
130	- 4	--	3.0
134	- 2	--	4.1
138	0	1.9	4.6
142	2	--	4.1
146	4	--	3.0
150	6	--	1.7
154	8	--	.8
158	10	<3.5[d]	.3
162	12	0	.1

[a] Azimuth from true north

[b] y-unit $\simeq$ 40 m

[c] Background value of 0.0035 μmol/ℓ subtracted. See Appendix A for details on determination of these values

[d] Two values obtained: 0 and 3.5.

concentrations in several uncontaminated plume area samples on Arc B. An apparent background concentration of methyl chloroform (no measurable background was seen for nitrobenzene) of 0.0035 μmol/ℓ (9 ng in the collected rain sample) has been subtracted from the determined concentrations. Using the value of α of 4.7 (Table 18), this corresponds to a gas phase concentration of 100 ng/ℓ or 17 ppb. This value is a factor of 4 greater than the average for source areas and a factor of 10 higher than the mean of all sampling points surveyed in a recent report (32). Thus, this apparent background may be due to some additional unidentified contamination source. In view of the analytical complications described in Appendix A, approximate error limits of ± 20% may be assigned these values.

Comparisons with Theory

Simulation of the field experiments by MPADD calculations were performed in the same manner as that described for the nitrobenzene test case in Section 3, with the following modifications.

- The spread parameters for the gaussian plume model were calculated from measured standard deviations of wind direction in the vertical (σ_ϕ) and horizontal (σ_θ),

$$\sigma_z = \sigma_\phi x \quad , \tag{19}$$

$$\sigma_y = \sigma_\theta x \quad . \tag{20}$$

- A real point source was employed (XUPW=0) at H=26m.
- The dry deposition velocity was arbitrarily set at 0.01 cm/sec (no significant effect on depletion in the study area).
- The y spacing of calculation points was set at the sampler spacing of 4°. For convenience, results are shown as "y-units", equal to the y distance corresponding to 4° angular spacing on the inner (200m) sampling arc.

- The raindrop size spectrum parameters were entered from actual measurements during the runs.
- Mathematical expressions for temperature dependency of diffusion coefficients derived by the methods in Reid and Sherwood (8) and solubility (Section 4) for methyl chloroform were employed for the run H3 simulation.
- The remaining input data for the runs from Tables 12 to 15 were used as appropriate.

Values of the diffusion coefficients and solubility parameters resulting in the simulations are shown in Table 18.

Table 16 and 17 and Figures 10-12 show the results of the simulations, along with observed concentrations in the collected rainwater samples. The error ranges on the observed values are based on errors in rain volumes collected during the light rainfall. For run H1, the error values for the MPADD results and the shaded regions in Figures 10-11 are based on the source-term error described in Appendix B. The measured very large values of σ_θ and σ_ϕ during Run H1-B (cf. Table 11) were considered unrealiable due to the often very low wind speed, so the data measured during released H1-A were used for the calculations shown here. Figures 10-12 show the observed and calculated concentrations for run H1 and H2 plotted against y-position (one y unit ~40 m). The centerline value of the calculated results is placed on the figure at the position relative to the observed values corresponding to the measured mean wind direction. Normal error in this measurement is ±5 degrees or about 1 y-unit. For Run H2, where Q is well known, the three calculation options for MPADD are shown for comparison. In addition to the standard, intermediate value, the upper curve represents

TABLE 18. PHYSICAL PROPERTIES OF HAP IN MPADD SIMULATIONS

Species	Run	T,K	Diffusion Coefficients cm^2/sec Liquid Phase	Gas Phase	Solubility α
Nitrobenzene	H1-A	276	8.8×10^{-6}	0.075	5703.
	H1-B	275	8.9×10^{-6}	0.074	6310.
	H2	279	9.0×10^{-6}	0.076	4211.
Methyl Chloroform	H3	280	9.6×10^{-6}	0.071	4.70

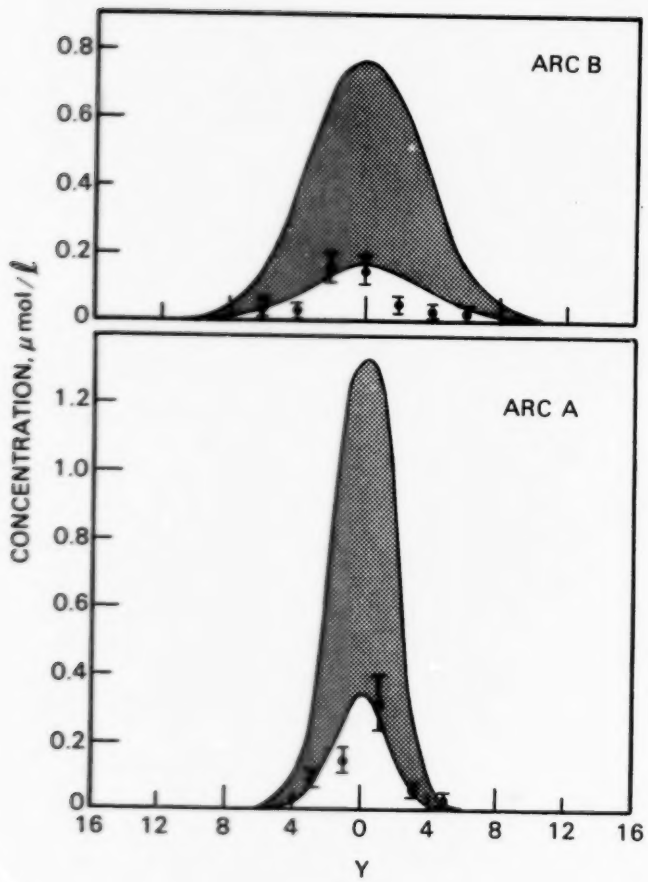

Figure 10. Observed and calculated rainwater concentrations, run H1-A. The shaded area represents the uncertainty in source term input to MPADD.

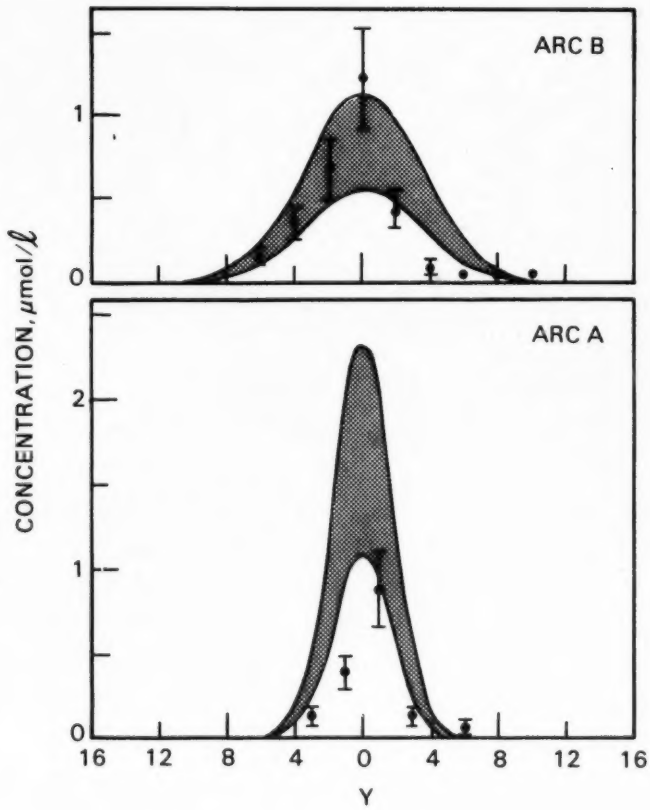

Figure 11. Same as Figure 10, but for run H1-B.

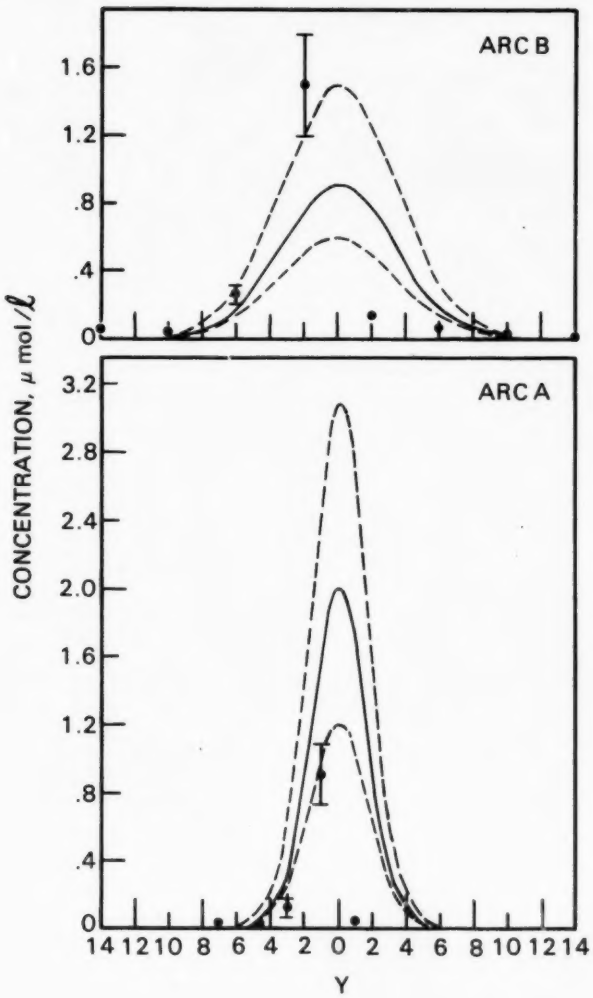

Figure 12. Same as Figure 10, but for run H-2. Three calculated curves represent the three mass-transfer options described in the test.

gas-phase controlled mass transfer (well-mixed drop), and the lower curve is for the stagnant drop case. These are considered to be the limiting cases for gas scavenging as affected by mass transfer (6) and real behavior should be somewhere in between. A similar range of calculated values applies to the cases of the other runs, but are not shown here.

The sparsity of observed concentration data for run H3 precludes determination of a deposition pattern. It is likely that this pattern, even under good analytical conditions, would be obscure due to the relatively high apparent background of methyl chloroform. It is encouraging, however, that the agreement with theory suggests that the effect of solubility on scavenging is handled well by the MPADD model.

Despite the uncertainty in source term input to MPADD for the H1 simulations, the agreement with the observed concentrations is good, especially for H1-B. There is a strong indication that the lower Q estimate for H1-A (and the corresponding higher Q for H1-B, since they are coupled) is more appropriate, but this is rather speculative since one cannot assume the model is true, and our only evidence for a lower Q during H1-A is intuitive. The unfortunate low sampler density for Run H2 decreases the accuracy of the comparison, since the observed deposition pattern was not well defined. The choice of plume parameters seems reasonable for all the nitrobenzene simulations, however, but it should be noted that agreement between model and observations should be more tenuous near the plume centerline, since the model results there are quite sensitive to σ_ϕ and σ_θ input. In addition, the peak of the deposition pattern may have been missed because of the location of

the samplers relative to the plume. The highest observed value for H2 on arc B appears inordinately high, since the concentrations should decrease with distance, following the diffusion of the plume as demonstrated by the model. We have no explanation for this apparent anomaly. The nearest collectors are probably quite far off the plume centerline, so we cannot determine if this is a true value. There was nothing unusual about the analysis or sample collection of this particular sample.

The cross-plume integrated flux comparisons should not include as great an error due to selection of plume parameters, since the air concentration dependence of the rainwater concentration is not strong for this "simple" gas, and for these downwind distances, which are far enough that desorption of gas from the raindrops "below" the plume is not significant. These fluxes W are shown in Table 16 for H1 and in Table 19 for H2. The calculated W for the intermediate mass-transfer option is always greater than the observed W, except for Run H2, arc B, which contained the possibly anamolous point. This suggests that the stagnant drop case may be the most appropriate mass-transfer description for nitrobenzene. Because of the various errors associated with the measurements and uncertainties in model input, no definite conclusion can be reached on this point. A similar result was obtained, however, with an experiment and calculations involving another simple solubility gas, HTO (33). Another source of considerable uncertainty arises from the strong temperature dependence of the solubility parameter α, as shown in Table 5. Small variations in the data or calculations used to determine this dependency can lead to large variations in α. For example, before the solubility data from the present project were

TABLE 19. Observed and Calculated Nitrobenzene (10^{10}), Cross-plume Integrated Fluxes (moles/cm sec x 10^{10}), Run H2.

ARC	OBSERVED	Calculated		
		Gas-phase	Intermediate	Stagnant Drop
A	1.1	6.7	4.0	2.6
B	4.5	6.4	3.8	2.5

available, MPADD simulations for Runs H1 and H2 were done using calculations based on vapor pressure data. These resulted in concentrations and cross-plume fluxes a factor of two less than those reported in this section.

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APPENDIX A

ANALYTICAL DETAILS FOR METHYL CHLOROFORM AND H3 RESULTS

Unanswered questions regarding the recovery of methyl chloroform at low levels from precipitation samples prompted the performance of several tests coincident with the field experiment H3. These tests included:

- Spiking two background samples with methyl chloroform and subjecting them to the same handling as field samples. Methyl chloroform (625 ng) was added to the pentane in the sample collection bottles before placing them in the field upwind of the release site. Although the amount added was large, the fact that they were open to the atmosphere ~1 hour longer than field samples and then stored and analyzed with these samples was intended to offer at least an indication of the relative magnitude of evaporative losses. The results obtained with two spiked blanks are recorded in Table A-1.
- Perchloroethylene was added to a limited number of samples after they were retrieved from the field. This addition was accomplished by syringe introduction of a 200 ppb methanol solution to the aqueous layer. The appearance of perchloroethylene in unspiked samples would signal contamination since this material is in common usage at Hanford. Recovery of less than 100% of the added material would appear to indicate volatilization during handling and/or inefficient extraction.
- Replicate analyses were conducted on several samples. Variation in analytical results over periods equal to or greater than the interval between sample collection and analysis would raise questions about sample integrity and provide information on the mechanisms acting to

TABLE A-1. RECOVERY OF METHYLCHLOROFORM FROM SPIKED BLANKS, H-3 EXPERIMENT

Sample	Added CH_3CCl_3, ng	CH_3CCl_3 Found, ng	Recovery, %
BKG - I	625	586	93.8
		579	92.6
BKG - II	625	562	89.9
		540[a]	86.4

[a] One day after initial analysis.

alter analyte concentration. Previous work with calibration standards stored in volumetric flasks at approximately 4 C indicate that pentane solutions of methyl chloroform are stable for periods of at least 8 days.

Initial processing of precipitation samples from experiment H-3 included the addition of 10 ml of pentane to assure ample solvent coverage during storage. In the period before work-up, these samples were stored in a refrigerator dedicated to precipitation sample storage. No other work involving halocarbons was conducted in the laboratories utilized and the preparation of standards was accomplished in an area isolated from sampling equipment and collected precipitation samples.

Samples from arc A were analyzed in a manner similar to that reported for nitrobenzene experiments. The only modification to this procedure was the addition of perchloroethylene to randomly selected samples and the analysis of the combined extracts and rinses without evaporation to concentrate the samples. The results of the initial perchloroethylene tests are recorded in Table A-2. They indicate that the recovery of this material is dependent on the amount present. Where 200 ng was added, 178 $\pm$ 17 ng (89 $\pm$ 8% recovery) was found after sample work-up. In contrast, recovery was 62 $\pm$ 7% when 100 ng had been added. The high mass of perchloroethylene found in A058, a sample to which only 100 ng had been added, could be attributed to contamination from a highly concentrated sample preceeding injection of this sample. Although the solvent flush technique was employed for sample injection, solvent blanks were run between samples in subsequent analyses as a precaution against cross-contamination. Another set of unspiked samples analyzed after those reported in Table A-2 did not show a problem with

TABLE A-2. RECOVERY OF PERCHLOROETHYLENE FROM SPIKED PRECIPITATION SAMPLES FROM EXPERIMENT H-3: APRIL 4, 1983 ANALYSIS

Sample	Added C_2Cl_4,ng	C_2Cl_4 Found,ng
A002	--	ND[a]
A010	--	13[b]
A018	--	ND
A130	--	ND
A114	--	ND
A034	200	161
A042	200	160
A050	200	199
BKG-I	200	184,184
B050	100	61,72
B058	100	55
A058	100	503[b]
A066	100	59

[a] None detected

[b] Measured perchloroethylene attributed to memory effect from previous sample containing a high concentration of the analyte.

cross-contamination. Precipitation which had been spiked with 100 ng of perchloroethylene showed 68.5 $\pm$ 2.9% recovery of the added material. Data from this set of samples is recorded in Table A-3.

The analysis of collected precipitation samples for methyl chloroform after experiment H-3 was delayed somewhat to complete the aforementioned tests on samples that were in general thought to be outside the region influenced by the HAP plume. Although this delay was recognized to lead to potential evaporative losses, the observed stability of well-sealed $CH_3CC\ell_3$ pentane solutions under refrigeration gave some assurance of maintaining sample integrity. However, as the analysis progressed it was apparent that rather than experiencing evaporative losses, contamination of collected samples was generally observed. Methyl chloroform found in arc A samples, reported in Table A-4:

- did not display a pattern which could be related to the observed wind data during release;
- did not correlate with perchloroethylene additions used to evaluate the extraction procedure;

and

- was inconsistent with cross-contamination via the glassware employed for sample work-up.

A few samples did not contain any observable methyl chloroform (detection limit $\sim$ 0.2 ppb or 6 ng per 30 mℓ of pentane extractent) which indicated that contamination was not uniformly observed or was masked by evaporative loses. Furthermore, since the analysis of pentane blanks including that used to charge the collection bottles before the experiment did not show detectable methyl chloroform, it appears that

TABLE A-3. RECOVERY OF PERCHLOROETHYLENE FROM SPIKED PRECIPITATION SAMPLES FROM EXPERIMENT H-3: APRIL 7, 1983 ANALYSIS

Sample	Added C_2Cl_4, ng	C_2Cl_4 Found, ng
A146	--	ND[a]
A154	--	ND
A162	--	ND
A130	--	ND, ND[b]
A138	--	ND
A114	--	ND, ND[b]
A122	--	ND
A106	100	69
A098	100	64, 73[b]
A090	100	68
A082	100	67
A074	100	67
A170	100	68
B070	100	72

[a] None detected

[b] Analyses conducted on consecutive days

contamination occurred during the period between sample retrieval and analysis.

In view of the contamination observed in samples subjected to the handling involved in the use of seperatory funnels for pentane extraction of methyl chloroform, the work-up procedure was modified for the analysis of the remaining samples. These samples, which included most of those collected on arc B, were opened only to withdraw an aliquot of the pentane layer for GC injection. Again methyl chloroform contamination was observed to be a common problem. In addition, carbon tetrachloride and a component with a retention time suggestive of trichloroethylene were observed in all samples. This contrasts with earlier analyses in which these materials were rarely observed. This observation would appear to suggest that both evaporation and contamination from an unknown source played a role in determining the final analyte concentrations reported in Table A-4. In contrast, the presence of carbon tetrachloride and trichloroethylene(?) in sample analyses reported in Table A-5 may be interpreted as indicating that evaporative losses had been minimized. Contamination was however encountered before analysis and continued to be a problem during the three day period in which analyses were conducted since several samples displayed an increase in methyl chloroform content between the first and second analyses.

The following conclusions and recommendations are made in the light of our experience with samples from a single methyl chloroform experiment.

TABLE A-4. CALCULATED MASS OF METHYL CHLOROFORM IN PRECIPITATION SAMPLES FROM EXPERIMENT H-3: APRIL 4-8 ANALYSIS

Sample	Collector Volume, mℓ	CH_3CCl_3,ng	Sample	Collector Volume, mℓ	CH_3CCl_3,ng
A002	90	52	B034	98	15
010	90	< 6	042	94	< 6
018	87	24	050	92	42,35
026	91	25	058	89	< 6
034	87	28	070	91	43
042	84	13			
050	79	24			
058	82	< 7			
066	81	< 6			
074	71	46			
082	78	22			
090	73	42			
098	72	35,30			
106	58	28			
114	72	28,25			
122	67	13			
130	68	10			
138	68	17			
146	63	6,20			
154	61	16			
162	64	30			

TABLE A-5. MASSES OF METHYL CHLOROFORM AND CARBON TETRACHLORIDE IN EXPERIMENT H-3 SAMPLES: APRIL 11-13, 1983 ANALYSIS

Sample	Collector Volume, mℓ	CH_3CCl_3,ng	2.35 min Peak Area	CCl_4,ng
B078	83	16;19	386;507	2;2
086	86	57;60	1241;1321	2;2
094	84	9;10	T[a];T	1;1
102	81	10;16	T;310	2;3
106	83	19;33	T;394	2;2
110	81	40;52	488;602	2;2
114	85	15;32	--;440	1;2
118	76	46;54	614;730	2;2
122	70	9;19	T,419	1;2
126	74	20;19	T,T	2;2
130	76	48;39	415,406	3;<1
134	72	19;36	425;703	2;2
138	76	15,14;17	T,T	2;2
142	73	56;61	501;662	2;<1
146	72	21;19	309;396	2;<1
150	70	15;16	409;360	2;2
154	59	64;67	720;932	3;<1
158	69	10;17	T;T	1;2
162	70	8;48	T;882	3;1
166	67	38;46	518,523	2;2

[a] Trace

- The sample bottles appeared to provide tight storage of the collected samples. This conclusion is supported by the absence of pentane loss during storage and the generally observed release of positive pressure when the bottles were opened for sample withdrawal.
- Cross-contamination which has been observed with septum capped storage containers (34) is not regarded as a significant contamination route here since the distribution of methyl chloroform should still display a profile consistent with the winds observed during the release.
- In the absence of a clearly defined source of contamination, the Teflon cap liners used to seal the sample bottles must be suspected. No attempt was made to avoid pentane contact with the liners and this contact was enhanced during mixing of the aqueous and solvent layers in the modified procedure for sample work-up.
- If this experiment were to be repeated, analysis should be completed within 24 hours of sample collection. The modified procedure for sample preparation in which an aliquot of solvent is removed from the storage bottle after mixing aqueous and solvent layers should be followed. Additional care should however be exercised in the selection of a cap liner and the procedure evaluated by running simulated samples.
- If one assumes that samples from arc B showing low concentrations of the component with a retention time of 2.35 minutes (trichloroethylene?) and carbon tetrachloride have experienced minimal contamination, peak concentrations in samples beneath the plume have an upper limit concentration of 4 ± 1 μmol/L.

APPENDIX B

CALCULATION OF SOURCE TERMS FOR FIELD RELEASES

Table B-1 shows the measurements and calculations required to calculate the source terms Q (moles/sec) for the field experiments by tank weight difference (±5%) and by observed liquid flow rate during the release (±15%). The latter error estimate is based both on small flow variations in actual flow and on visibility of the flow meters on the video screen.

The Run H1 source terms are a special case since due to the separation of the nitrobenzene/hexane mixture, the mass of nitrobenzene released during each part of the run cannot be determined from the two methods above. The mass concentration of nitrobenzene in the mixture almost certainly varied from one release to the other. The flow rate method cannot be used directly because

- indicated flow rate is a function of density and viscosity of liquid
- very low flows were experienced during H1-A

The normal tank mass method (Table A-1) provided only a measure of total mass of nitrobenzene plus hexane. The concentration of nitrobenzene remaining thus had to be determined analytically. This was done later, and the concentration of the mixture was found to be 0.20 g nitrobenzene/cm^3 solution. If M_N and M_H are the remaining masses of nitrobenzene and hexane, the corresponding volumes are V_M and V_H, and their respective densities are 1.2 and 0.66 (kg/ℓ), we can form and solve the following four equations:

$$\frac{M_N}{V_N} = 1.2; \quad \frac{M_N}{V_H} = 0.66; \quad M_N + M_H = 7.2 \text{ kg}; \quad \frac{M_N}{V_N+V_H} = 0.2. \qquad (21)$$

TABLE B-1. SOURCE TERMS, FIELD EXPERIMENTS (kg)

		Mean Run H1	Run H2	Run H3
Mass Method				
Mass of Pressure Tank	kg	50.2	48.4	11.4
Mass of Solvent	kg	9.9	10.4	0
Mass of HAP	kg	3.3	3.3	8.1
Total	kg	63.4	62.1	19.5
Total Mass of Tank, post release,	kg	57.4	51.9	12.4
Difference	kg	6.0	10.2	7.1
Mass fraction of solute		---	.24	1.0
Mass of HAP released,	kg	1.4[a]	2.4	7.1
Flow Method				
Average Liquid Flow Rate	ℓ/min	.24 ± .04	.5 ± .075	.175 ± .025
Time of Release, min		32	29	32
Liquid flow total, ℓ		7.7 ± 1.3	14.5 ± 2.0	5.6 ± 0.8
Volume fraction of solute		.14	.16	1
HAP Flow total, ℓ		1.1 ± .2	2.3 ± .4	5.6 ± 0.8
HAP density, kg/ℓ		1.2	1.2	1.3
Mass Released	kg	1.3 ± .2	2.8 ± .4	7.3 ± 1.1
Molecular weight		123	123	133
Q[b], moles/sec		0.0058	0.011	0.028

[a]Determined from post analysis, see text

[b]Mass method result used: ± 5%

The solutions are: M_N=1.9 kg; V_N=1.6 ℓ; M_H=5.24 kg; V_H=7.94 ℓ. Thus the mass of nitrobenzene during both H1 releases was 1.36 kg, and the total volume of solution released was 8.3 ℓ.

Knowing this, we can attempt to calculate the mass of nitrobenzene released during each part of the experiment, considering the other known or estimable quantities - namely the release times and liquid flow rates. In the following, subscripts A and B refer to releases H1-A and H1-B, respectively, M is the mass of nitrobenzene released, C is the mass concentration of nitrobenzene in the releases solution, V is the volume of solution released, F is the liquid flow rate, and T is the time of release. The masses released are

$$M_A = V_A C_A = F_A T_A C_A \qquad (22a)$$

$$M_B = V_B C_B = F_B T_B C_B \ , \qquad (22b)$$

the total volume released was

$$T_A F_A + T_B F_B = 8.3 \ , \qquad (22c)$$

and the total mass of nitrobenzene is

$$M_A + M_B = 1.36 \ . \qquad (22d)$$

Equation (22c) can be solved for one flow rate if we know the other and the flow times. The flow rate for part B is reasonably well known, and is .300±.04 ℓ/min, if it is assumed that the solution density and viscosity is about the same as methanol (0.8 g/ml) (original release mixture density = .74), for which the flow meters were calibrated. The flow meter calibration curves are shown in Figure B-1. The flow rate for part A is poorly known from flow meter observations, as the flows were very near the bottom of the meters, but it is clear that the flow F_A is at least a factor of two below F_B, even for a denser liquid. The solution for (22c) is shown in Figure B-2, given T_A=11 min, and T_B=21

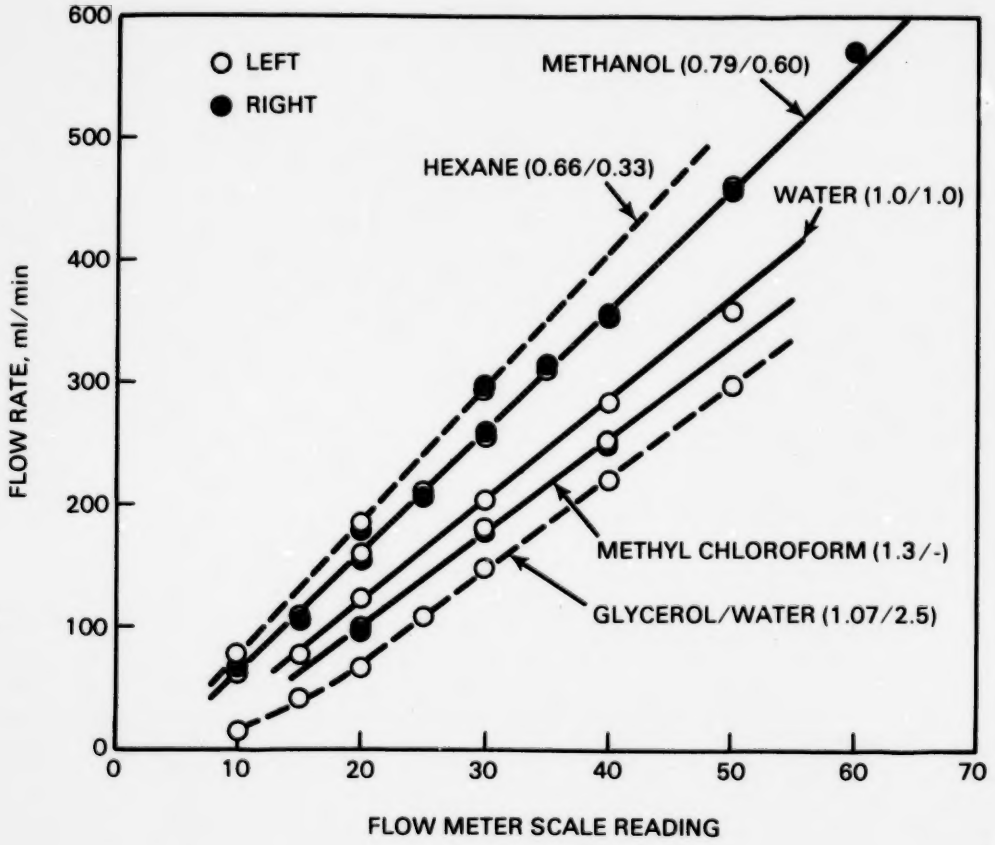

Figure B-1. Calibration curves for AALBORG (Cell No. FM044-40, 150 full scale) flowmeters. Numbers in parenthesis are (specific gravity (g/cm^3)/ viscosity (cp)).

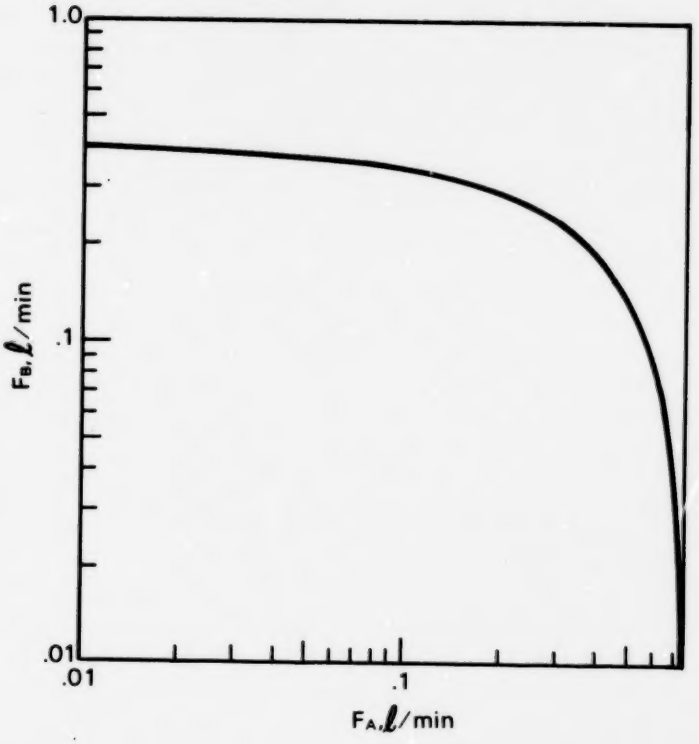

Figure B-2. Solution to equation (22c).

min. Clearly, the uncertainty in F_A is much greater than in F_B, namely .180±.08 ℓ/min (±45%). The flow solution is critical to the solution of (22), and it is clear that our normal error in flow measurements for part B is not sufficient for resolving the source terms, since we cannot estimate the mass densities C with any certainty. We can, however, make some estimates of the density ratio $\beta=C_B/C_A$ and combine with the flow ratio $\gamma=F_B/F_A$ to arrive at limiting values for the source term ratio, which is $\gamma\beta$ (i.e., $\gamma\beta = C_BF_B/C_AF_A = M_BT_A/M_AT_B = (M_B/T_B)/(M_A/T_A)$.

Table B-2 shows estimates for the various quantities, based on examination of equations (22) and qualitative assessments of the degree of separation of the solutions during the two releases. The worst limiting case is that for minimum β. The β observed for the two layers found in the remaining solution, several days after the release, and at comparable temperature to that during the release H1-A, was 0.13. We feel that β was not likely to have been less than this for H1-A. The result is close to what might be considered the first-order estimate, namely the mean Q for both parts, 5.8×10^{-3} m/sec (Table B-1), but with large uncertainty. Therefore, the source term used for model comparisons ("best") is this value, recognizing that a factor of two variation is possible for H1-A, and somewhat less for H1-B.

TABLE B-2. ESTIMATES FOR SOURCE TERM RATIO, RUN H1

	γ	B	γB	Q_B moles/sec	Q_A $\times 10^3$
Minimum	2	.13	.26	2.9	11.2
Maximum	4	1	4	7.8	3.1
Mean (Range)				5.4 ($\pm$45%)	7.2 ($\pm$55%)
Best (Range)				5.8 ($\pm$30%)	5.8 ($\pm$60%)

APPENDIX C

Rain Volumes and Nitrobenzene Masses
From Field Experiments H1 and H2

TABLE C-1. COLLECTED RAIN VOLUMES, EXTRACTION EFFICIENCIES, AND MASSES OF NITROBENZENE RUN H1.

Sample	Position[a]	Volume, ml	Indicated $C_6H_5NO_2$, ng	Extraction Efficiency[b] %	Corrected mass[c], ng
A	034	54		(75)	
	042	52		(75)	
	050	51	2.2	89	2.5
	058	54	--	--	
	066	52	--	--	
	074	50	--	(75)	
	082	54	< 1.5	78	< 2.
	090	51	< 1.5	(75)	< 2.
	098	56	45.4	64	71
	106	50	147	74	199
	114	54	453	100	453
	122	53	54.4	74	74
	130	53	26.3, 24.3	(75)	34
	138	52	51.6, 59.1, 59.5	97	58
	146	52	80.7, 84.8	71	117
	154	52	16.9	(75)	23
	162	53	9.7, 13.4	100	12
B	094	50	< 1.5	82	< 2.
	098	51	19.2	28	69
	102	52	140	79	177

(Table C-1 continued)

Sample Position[a]	Volume,ml	Indicated $C_6H_5NO_2$,ng	Extraction Efficiency[b] %	Corrected mass[c],ng
106	54	243	75	324
110	52	429	68	631
114	53	133	60	222
118	45	34.5, 30.7	77	42
122	50	14.9, 18.3	75	22
126	47	12.3, 13.2, 13.4	88	15
130	56	10.1	60	17
134	54	9.4, 10.2	81	12
138	57	23.3, 22.6	42	55
142	55	47.7, 40.8	(75)	59
146	55	34.7, 37.4	53	68
150	54	16.7, 17.5	96	18
154	46	7.1, 9.4	89	9.3
158	52	4.7, 7.0, 7.0	73	8.5
162	54	< 1.5	75	< 2.

[a] Azimuth from true north, degrees.

[b] Numbers in parenthesis were not measured, but are assumed to be the mean of 75 ± 17%.

[c] Indicated mass/extraction efficiency.

TABLE C-2. COLLECTED RAIN VOLUMES AND MASSES OF NITROBENZENE, RUN H-2

Sample Position[a]	Volume, ml	Indicated $C_6H_5NO_2$, ng	Corrected[b], ng
A 098	216	33.8	45
106	191	35.2	47
114	214	34.4	46
122	206	245, 347, 279	390
130	210	2040, 2280	2880
138	210	80.2	107
BKG - I	225	< 1.5	< 2.
BKG - II	223	< 1.5	< 2.
B 106	221	173	231
114	226	78.2	104
122	210	632	843
130	235	3830, 3720	5030
138	228	566	755
146	220	147	196
154	206	99.9	133
162	209	3.3	4.4

[a] Azimuth from true north, degrees

[b] Due to interfering contamination, extraction efficiencies were not determined. Used was the mean from run H-1 of 75 $\pm$ 17%.